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MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-**TP**-1998-097
Mario Fajardo and Simon Tam "Solid Parahydrogen" **HEDM Conference Presentation** **(Statement A)**

HIGH ENERGY DENSITY MATTER CONTRACTORS CONFERENCE
Monterey, CA 20-22 May 1998.

Solid Parahydrogen

Mario E. Fajardo and Simon Tam
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Introduction

- Atom Doped Cryogenic Solid Propellants
- Laser Ablation/Matrix Isolation Spectroscopy
- Rapid Vapor Deposition of Thick Transparent pH_2 Solids!
  - ortho/para Hydrogen Converter

Research Update

- Microscopic Structure of Rapidly Deposited pH_2 Solids
  - IR, Raman, x-polarizers
- MIS Spectroscopy in Doped pH_2 and oD_2 Samples
  - "High Resolution" IR Absorption Measurements
    - CH_4/pH_2, CH_3OH/pH_2
  - Application: CO/pH_2 -- a Molecular Thermometer
  - Photochemistry (guest-host reactions)
    - O_2/pH_2, B_2H_6/oD_2
  - Photodynamics (LIF and photobleaching)
    - B/pH_2, B/Ne, Na/pH_2, Na/Ne

Conclusions and Future Directions

- High Resolution IR Spectroscopy in pH_2 Hosts

High Energy Density Matter (HEDM) Cryosolid Propellants

Objectives

* Trap 5% molar concentration of energetic additives in solid hydrogen.
* Demonstrate size-scaleable sample production method.

Payoffs

<u>Increased Specific Impulse</u>

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$\text{LOX/LH2} : I_{sp} = 390 \text{ s}$$
$$5\%\ B/H_2 + \text{LOX} : I_{sp} = 500 \text{ s } (+30\%)^*$$

* calculated for $P_{chamber} = 1000$ PSIA, $P_{exhaust} = 14.7$ PSIA

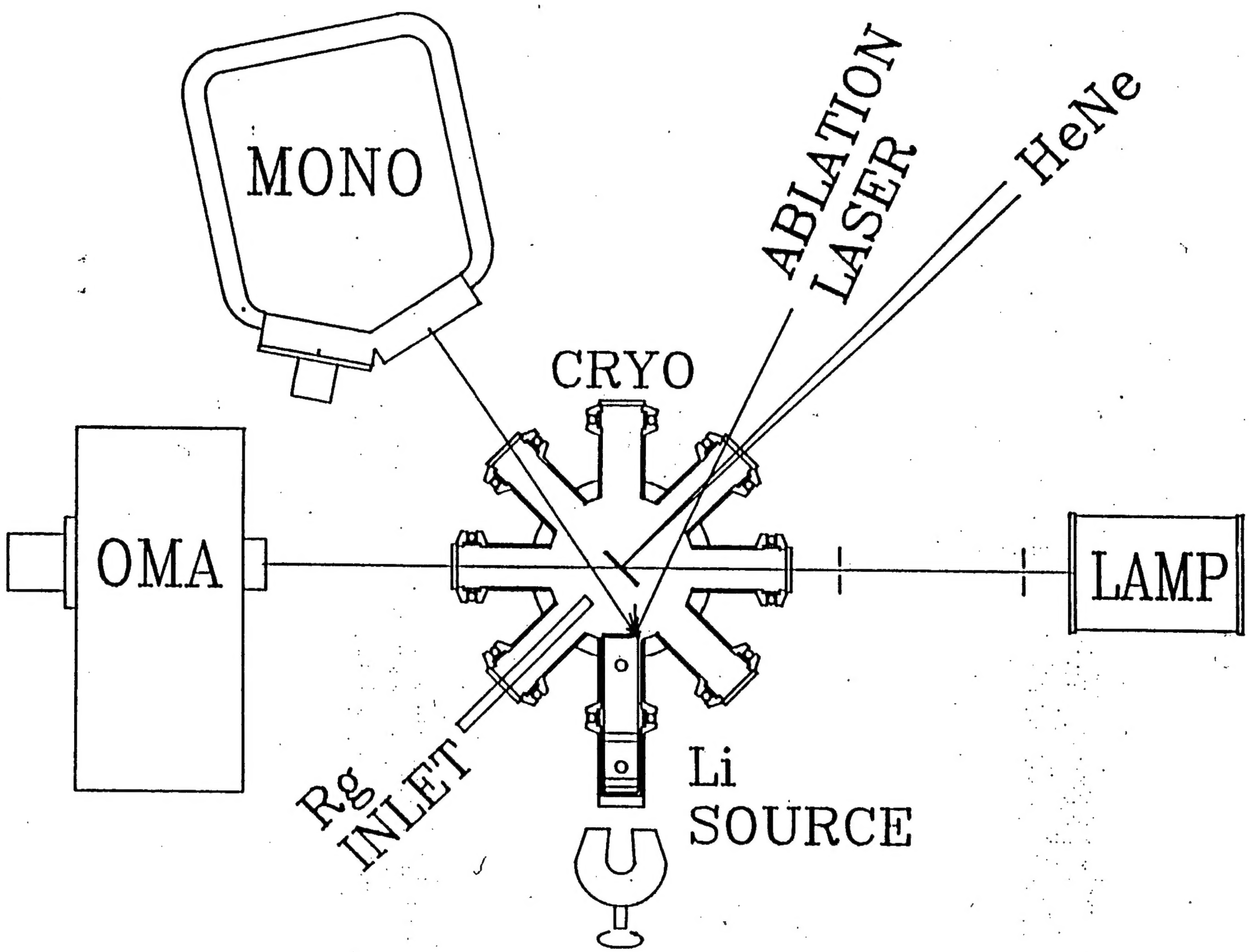
<u>Greater Propellant Density</u>

$$\text{liquid } H_2 \text{ @ } 20 \text{ K} : \rho = 0.070 \text{ g/cm}^3$$
$$\text{solid } H_2 \text{ @ } 2 \text{ K} : \rho = 0.087 \text{ g/cm}^3 \ (+25\%)$$
$$\text{50/50 liquid He/solid } H_2 : \rho = 0.105 \text{ g/cm}^3 \ (+50\%)$$

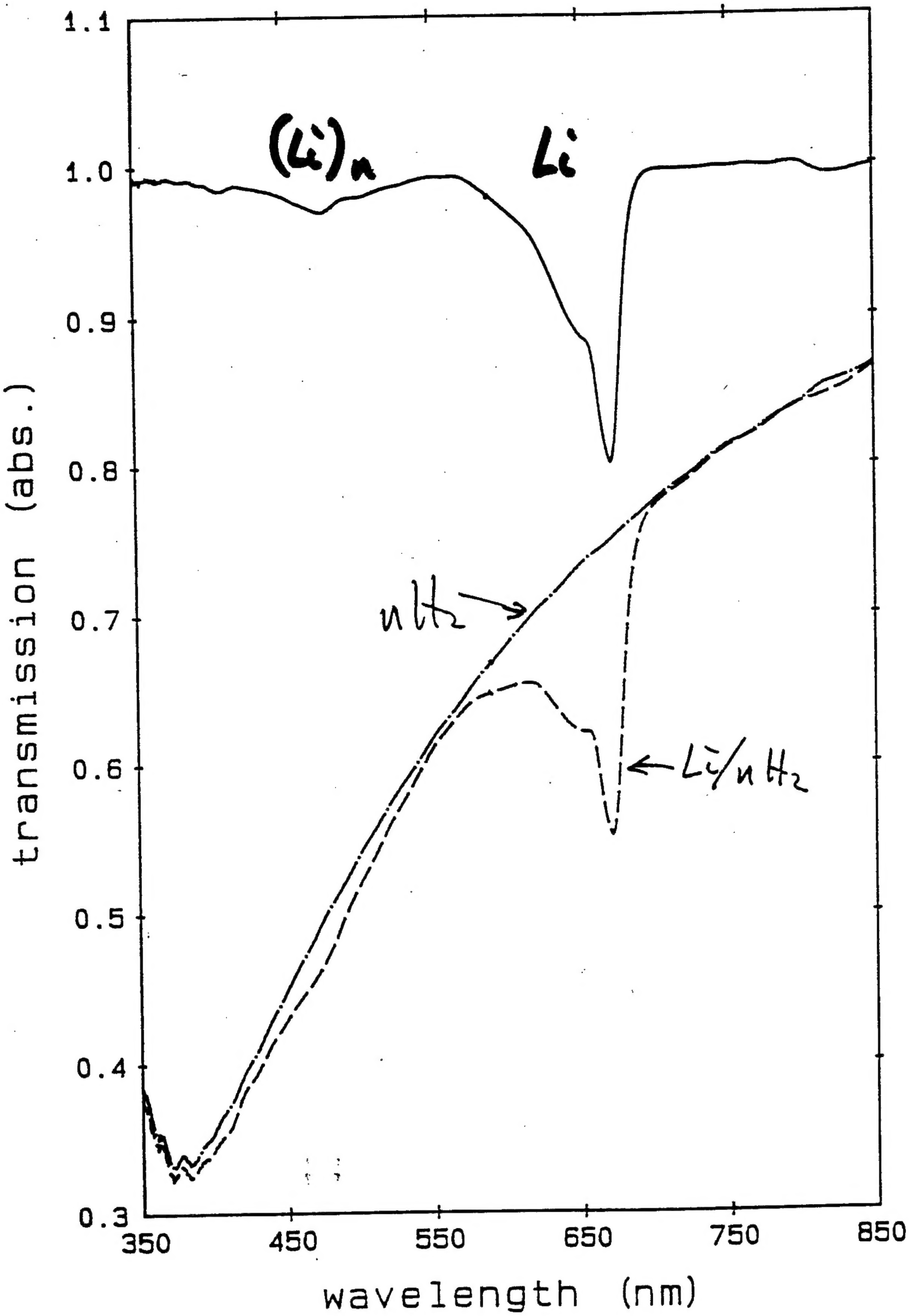
Scientific/Technological Motivations

Issue	Scientific Motivation	Tech. Application
Chemical stability of M/pH_2 samples	Chemical reactivity @ low T (1-10 K) existence of small reaction barriers in $M + H_2$ reaction matrix host effects	Identify candidate M's
Microscopic model of sample deposition process	Molecular dynamics of "simple" condensed phase systems (models for more complicated chemistry)	Maximize [M]
Simulation of M/RGS and M/pH_2 spectroscopy	Spectroscopy in condensed phases spectrum $\leftrightarrow$ structure/fluctuations	Measure [M] and determine fuel ρ
Diffusion/recombination of M's	Diffusion in "classical" and "quantum" solids	Determine thermal stability of M/H_2 fuel
Maximum attainable [M]	Limits of chemical energy storage	fuel performance

Experimental Diagram



Li/H_2 T=3K



M.E. Fajardo, J. Chem. Phys. 98, 110 (1993).

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

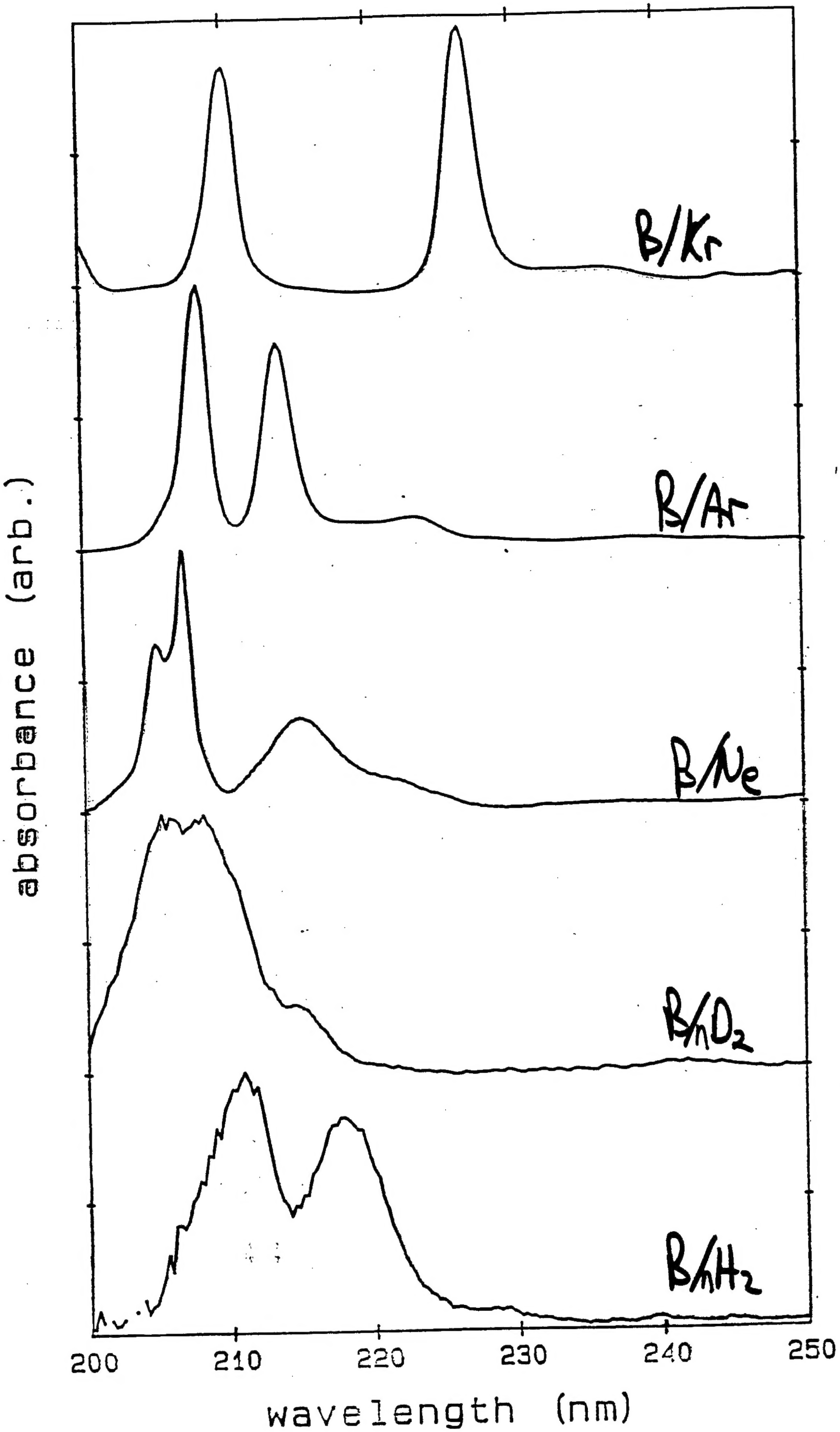
"There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow."

Crystallite Light Scattering (p. 83)

"The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

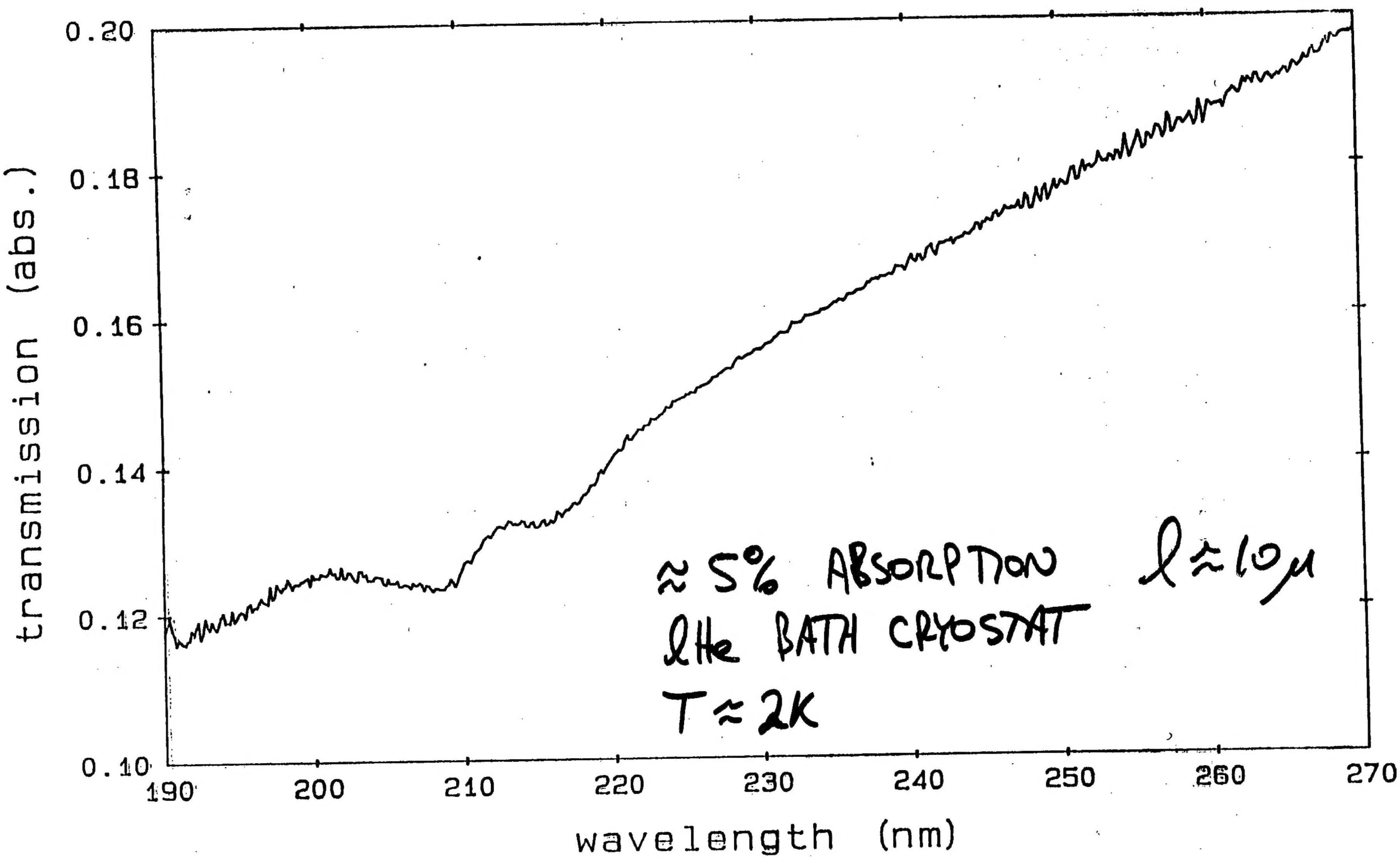
Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black."

P.C. Souers,
Hydrogen Properties for Fusion Energy
(UC Press, Berkeley, 1986).

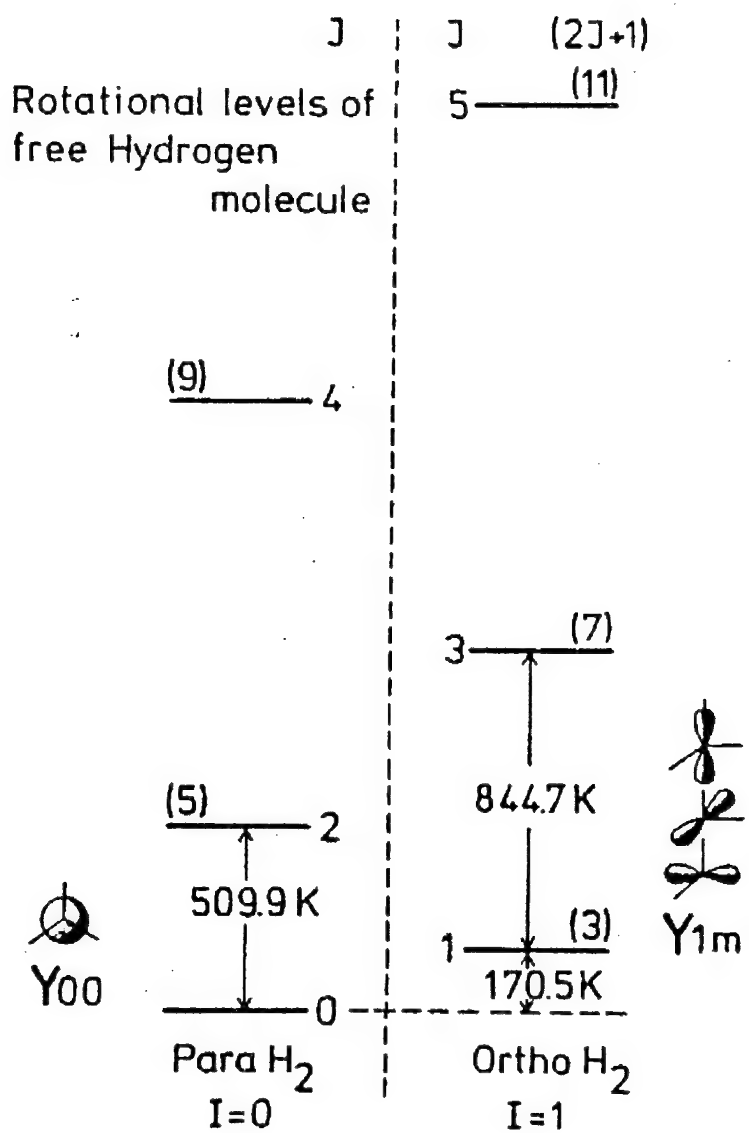


S. TAM + M.E. FAJARDO, UNPUBLISHED.

B/n-H2 raw data (c1993)

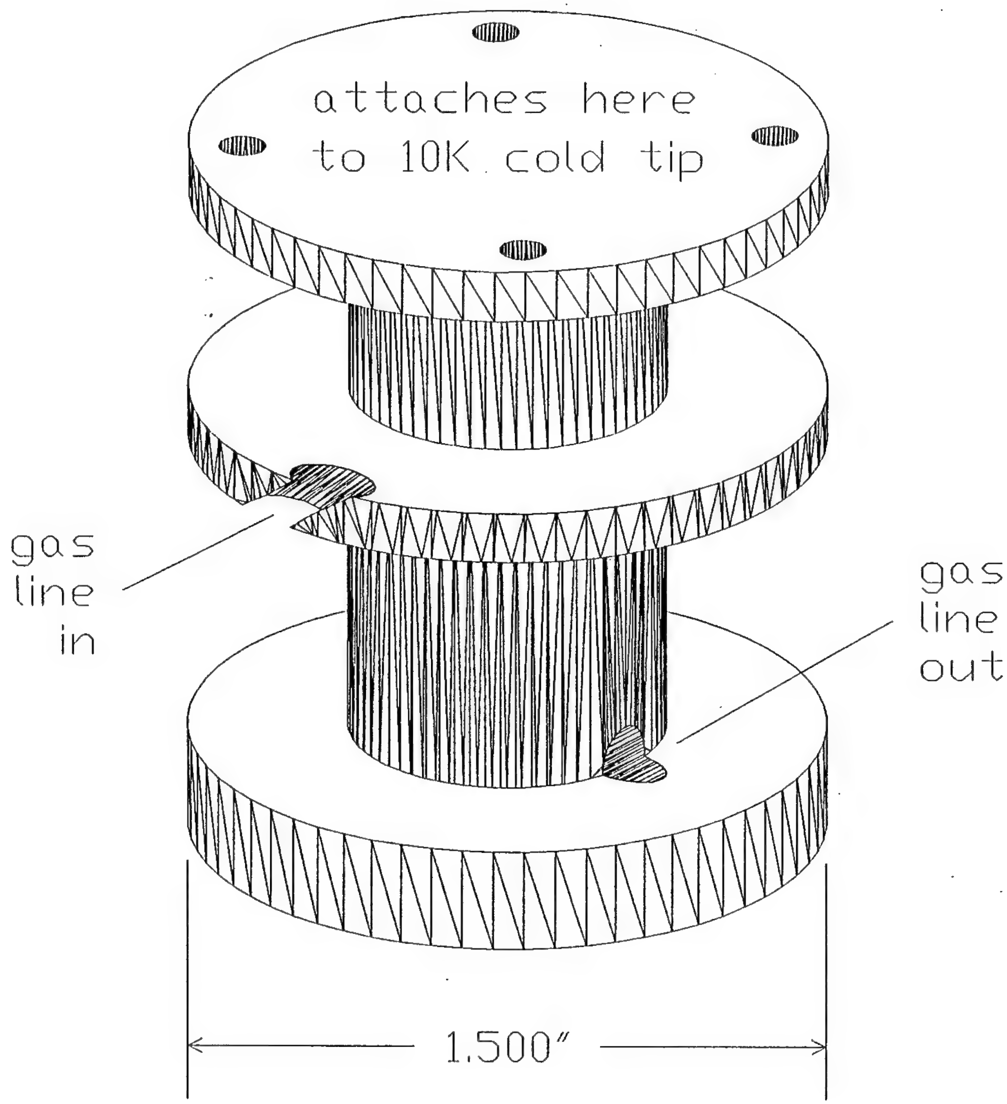


Ortho and Para Hydrogen



I.F. Silvera,
Rev. Mod. Phys. **52**, 393 (1980).

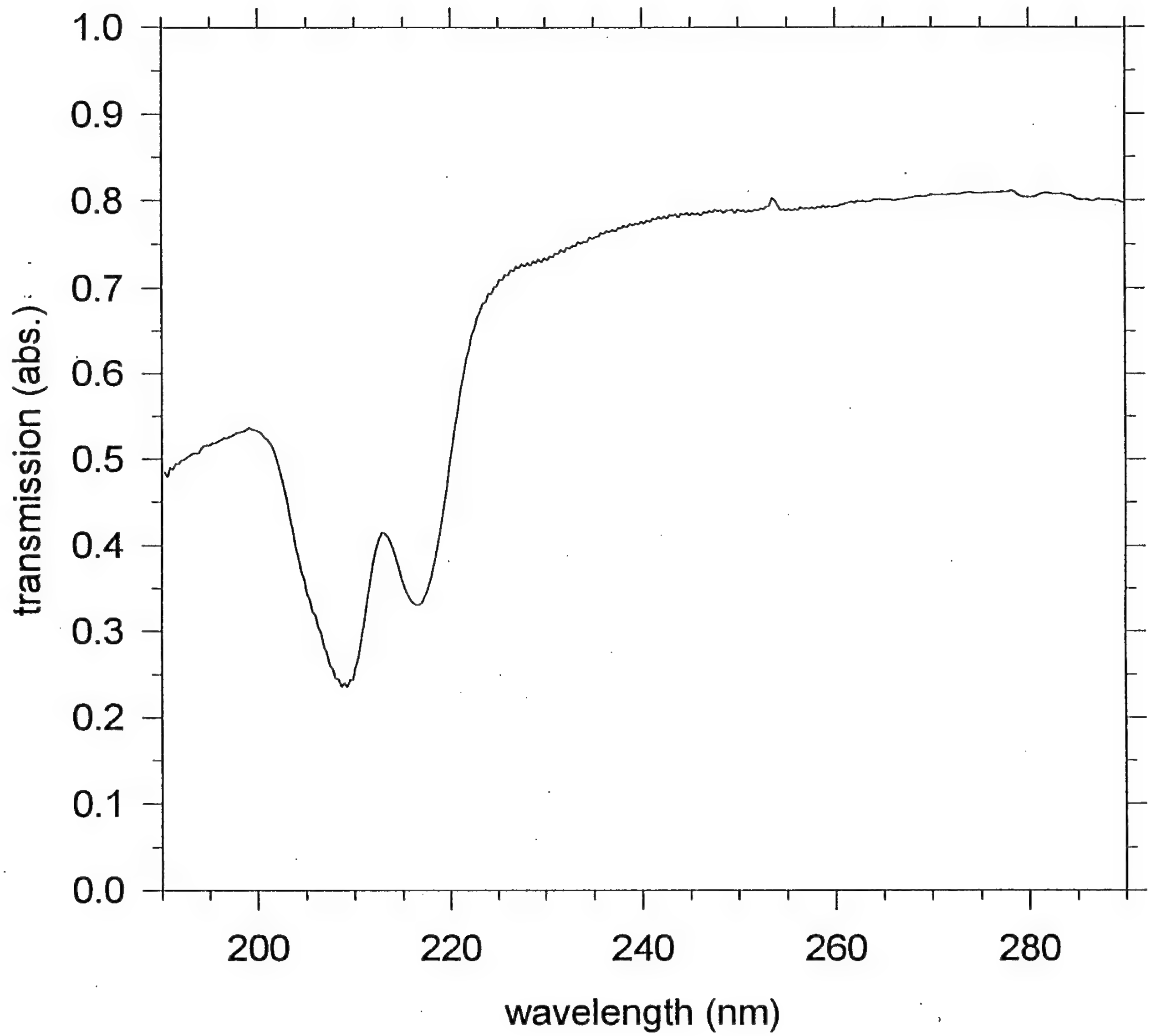
Ortho/Para Hydrogen Converter Bobbin



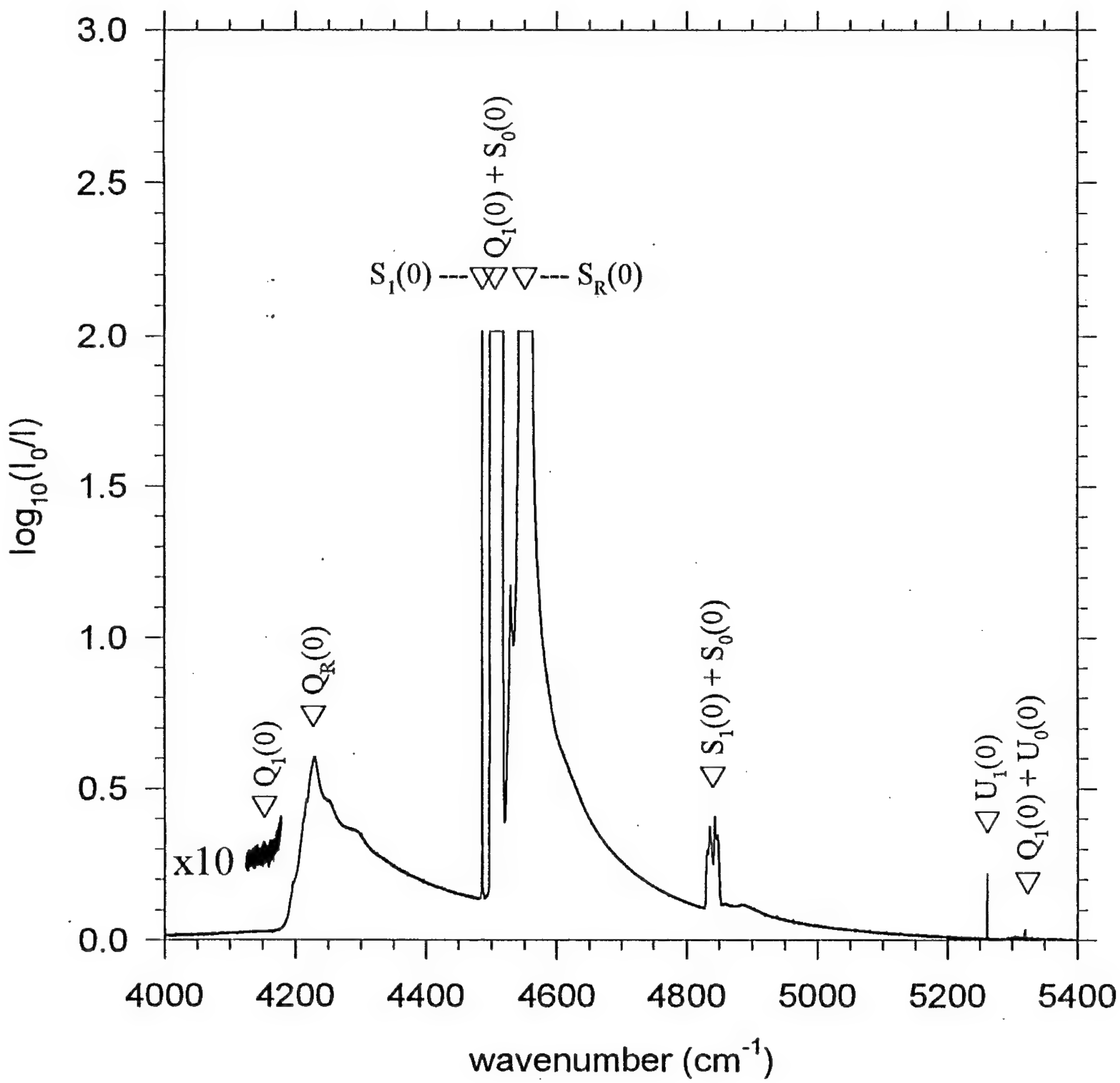
1/8 inch OD by 1.5 m long copper tube packed with 1.4 g of APACHI catalyst, coiled around bobbin and potted in place with metal-filled thermally conductive epoxy.

Catalyst is activated by heating to 150 °C under vacuum, then with a slow flow of H_2 gas.

UV Transmission of 1 mm Thick B/pH_2 Sample



IR Absorption of 6 mm Thick Parahydrogen Solid



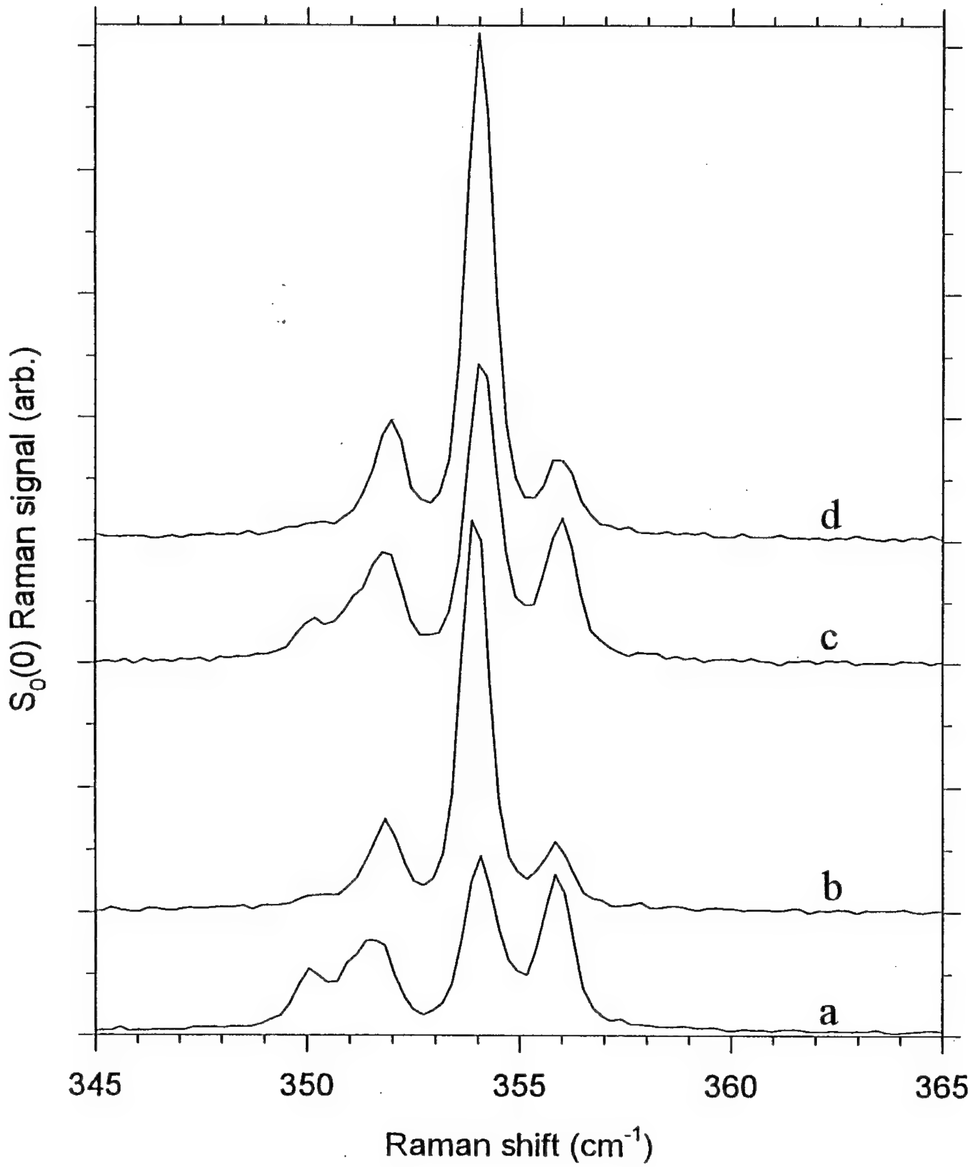
T = 2 K.

Non-observation of the $Q_1(0)$ transition (4153 cm^{-1}) demonstrates the absence of oH_2 impurities, and that the microscopic structure is not amorphous or porous.

Observation of $S_1(0)$ transition demonstrates the absence of inversion symmetry for some H_2 molecular environments.

[J. van Kranendonk and H.P. Gush, Phys. Lett. **1**, 22 (1962)]

Raman Spectra of 4.5 and 6 mm Thick Parahydrogen Solids



Mixed hcp/fcc as-deposited structure, anneals to hcp; compare with:

G.W. Collins, et al.,
Phys. Rev. B **53**, 102 (1996).

(d) sample in (c) warmed to 4.5 K.
(c) 4.5 mm sample as deposited at 3.3 K ($\Phi = 290$ mmol/hr).

(b) sample in (a) warmed to 4.5 K.
(a) 6 mm sample as deposited at 3.1 K ($\Phi = 200$ mmol/hr).

Infrared spectroscopic study of rovibrational states of methane trapped in parahydrogen crystal

Takamasa Momose,[a] Masaaki Miki, Tomonari Wakabayashi, and Tadamasa Shida
Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-01, Japan

Man-Chor Chan,[b] Steven S. Lee, and Takeshi Oka
Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

(Received 23 June 1997; accepted 15 August 1997)

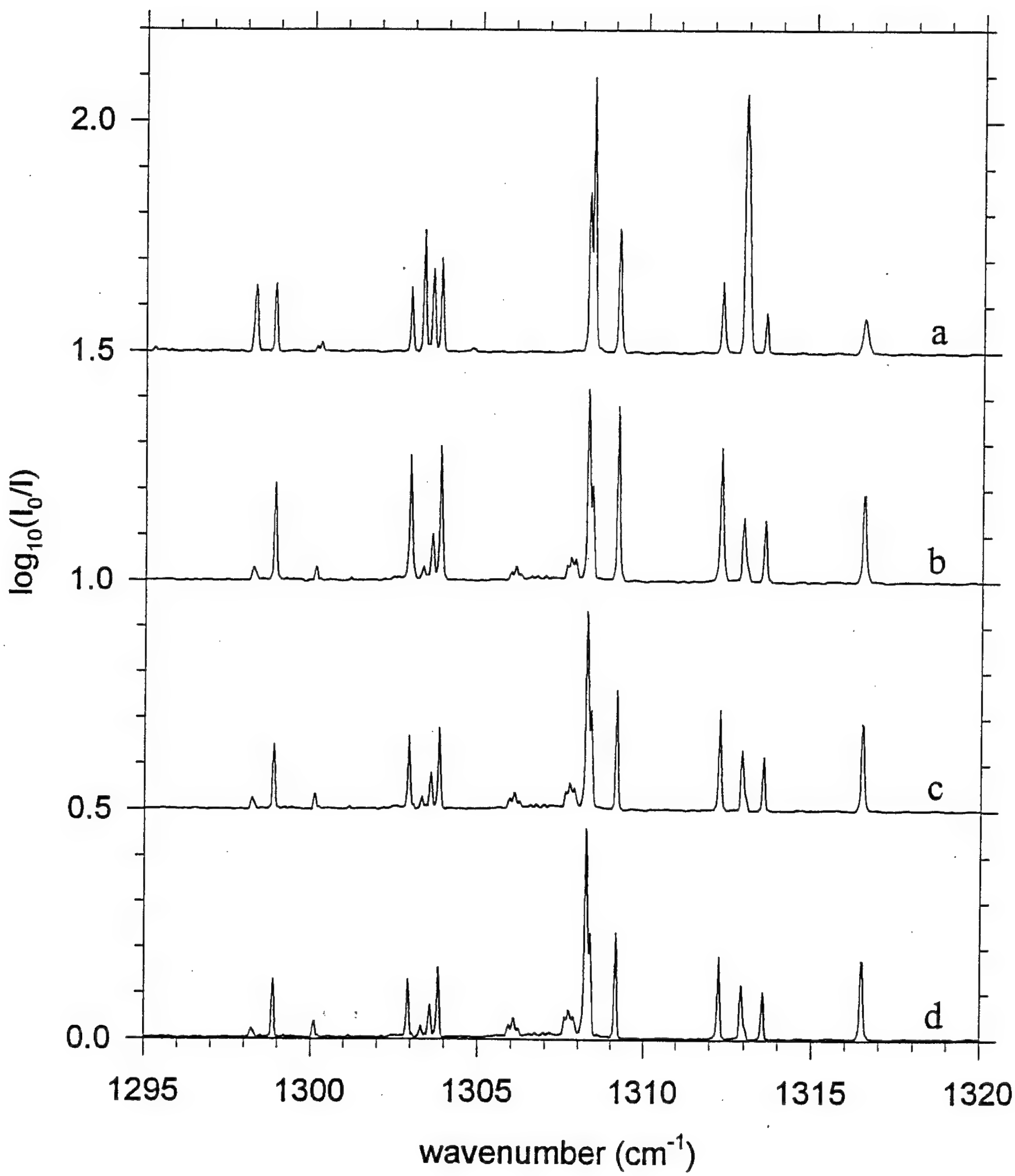
The ν_3 and ν_4 vibrational transitions of methane trapped in solid parahydrogen have been observed by using Fourier transform infrared and high resolution laser spectroscopy. The observed spectrum is interpreted in terms of rovibrational states of the spherical rotor which are subjected to the crystal field splitting. The ν_4 band shows extremely sharp lines of a width of $\sim 0.003\ \mathrm{cm}^{-1}$, while the ν_3 band exhibits broader lines of a width of $1\ \mathrm{cm}^{-1}$. The infrared selection rules derived from an extended group theory to take into account the field effect are consistent with the observed spectra. The intermolecular interaction and the field effect in solid parahydrogen are analyzed quantitatively.
 [S0021-9606(97)04743-0]

JCP 107, 7707 (1997)

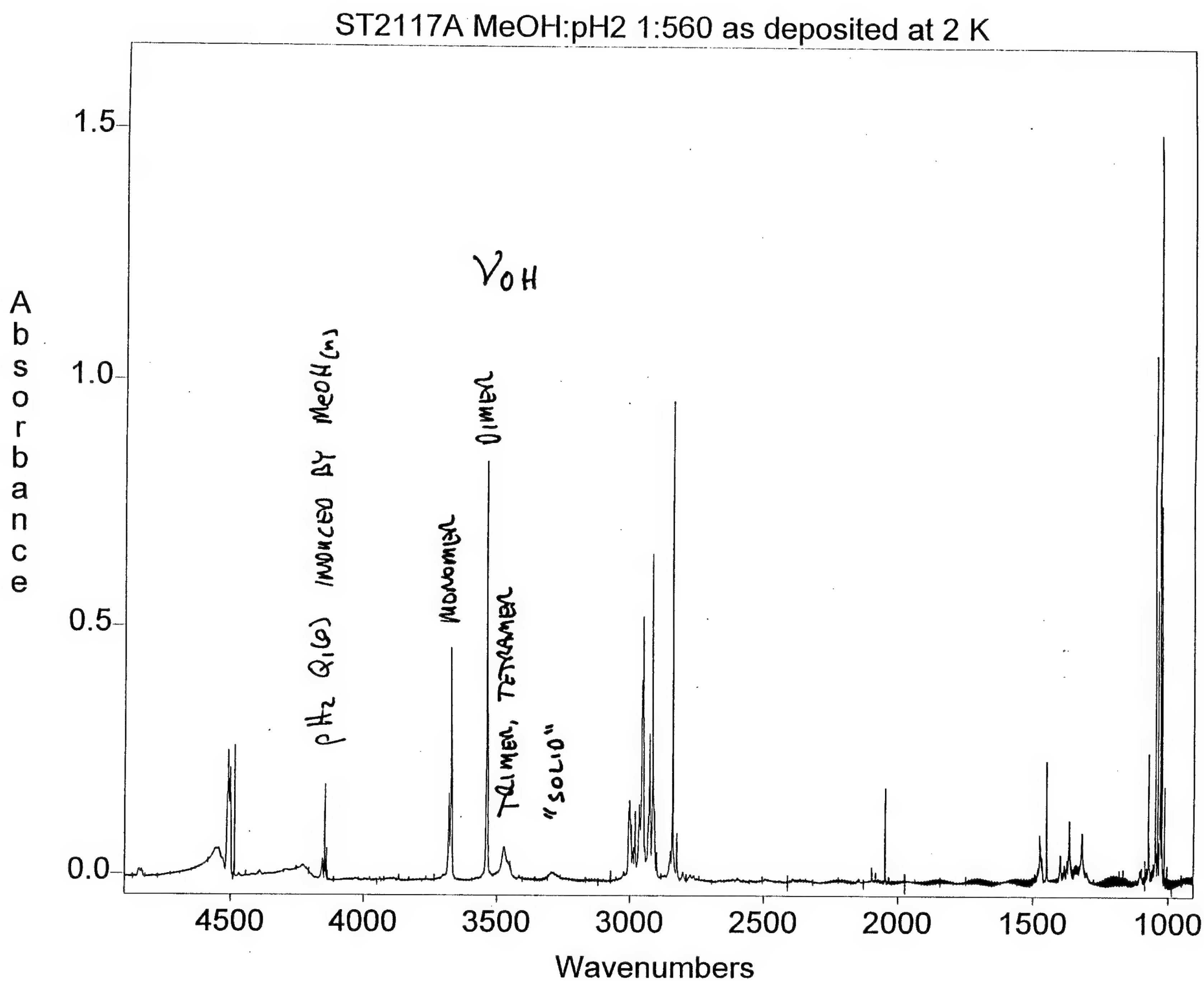
110 PPM CH_4/pH_2, d = 1.2 mm

st2320a: as dep. T=2 K

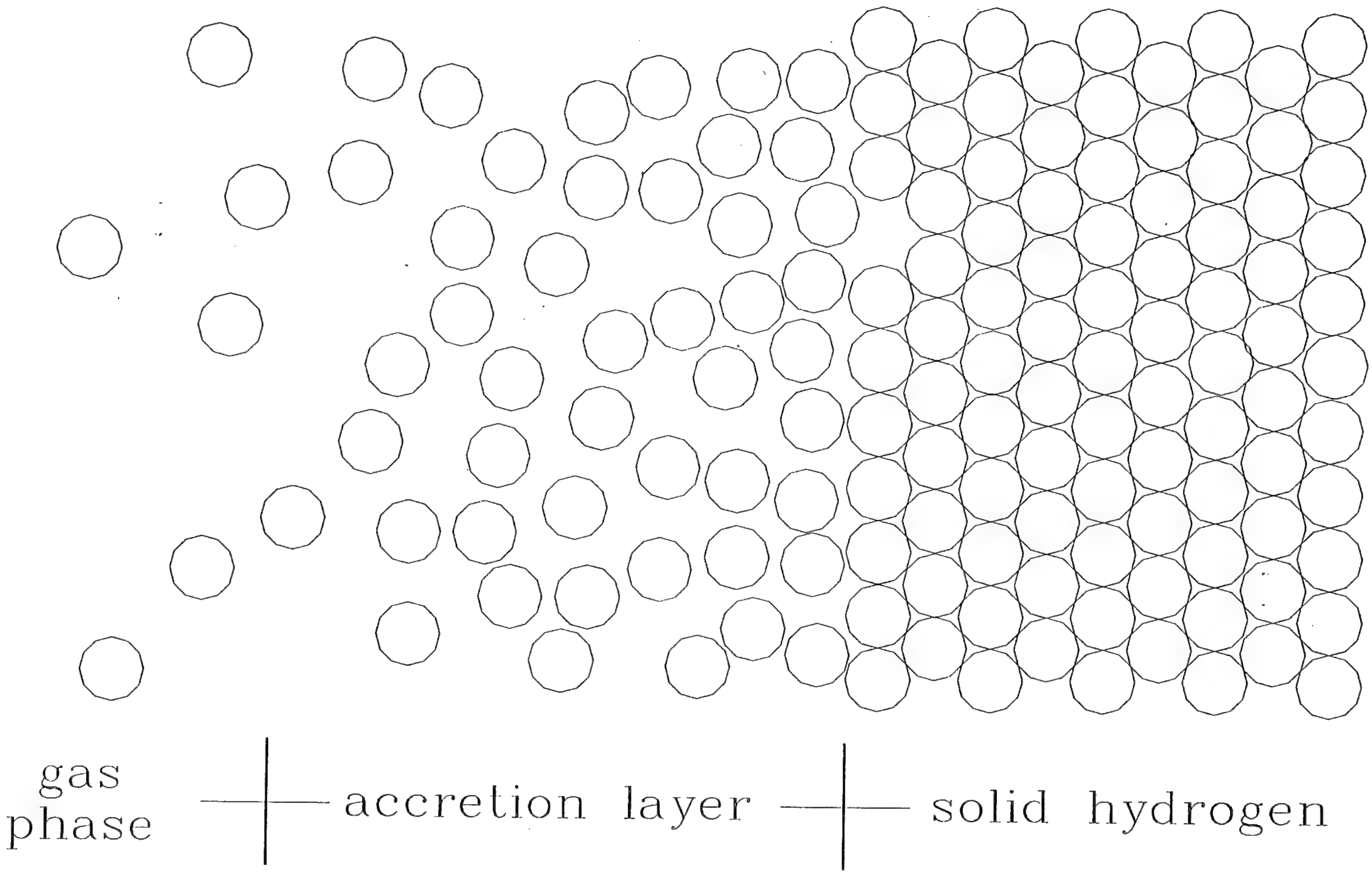
b: 4.4K, c: 3.0K, d: 2.2K



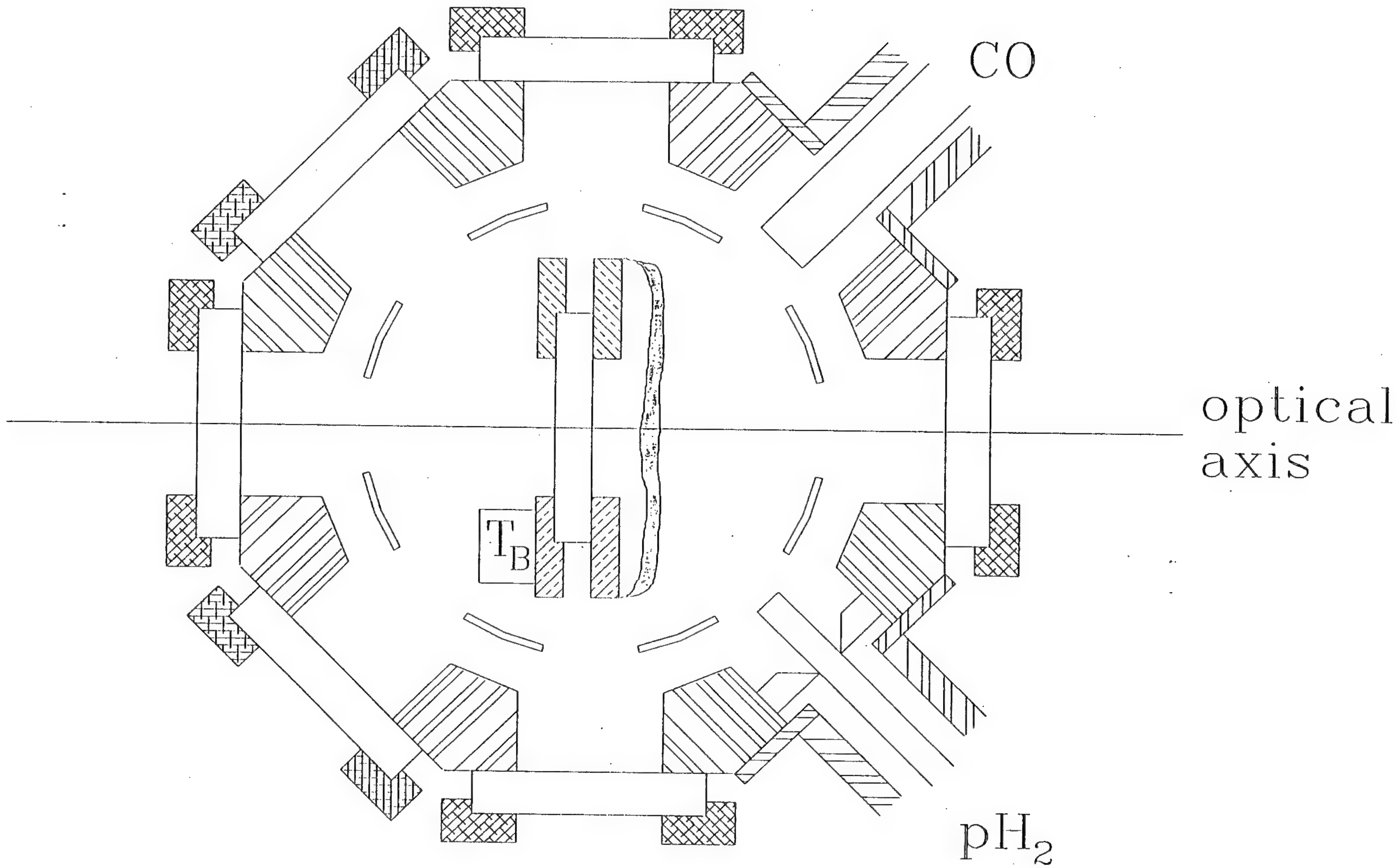
c:\mef\datash2\methane\st2320.spw


ST2117A MeOH:pH2 1:560 as deposited at 2 K
Absorbance
1.5
1.0
0.5
0.0
4500
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
ν_{OH}
pH2 Q1(0) INDUCED BY MEOH(n)
MONOMER
DIMER
TRIMER, TETRAMER
"SOLID"

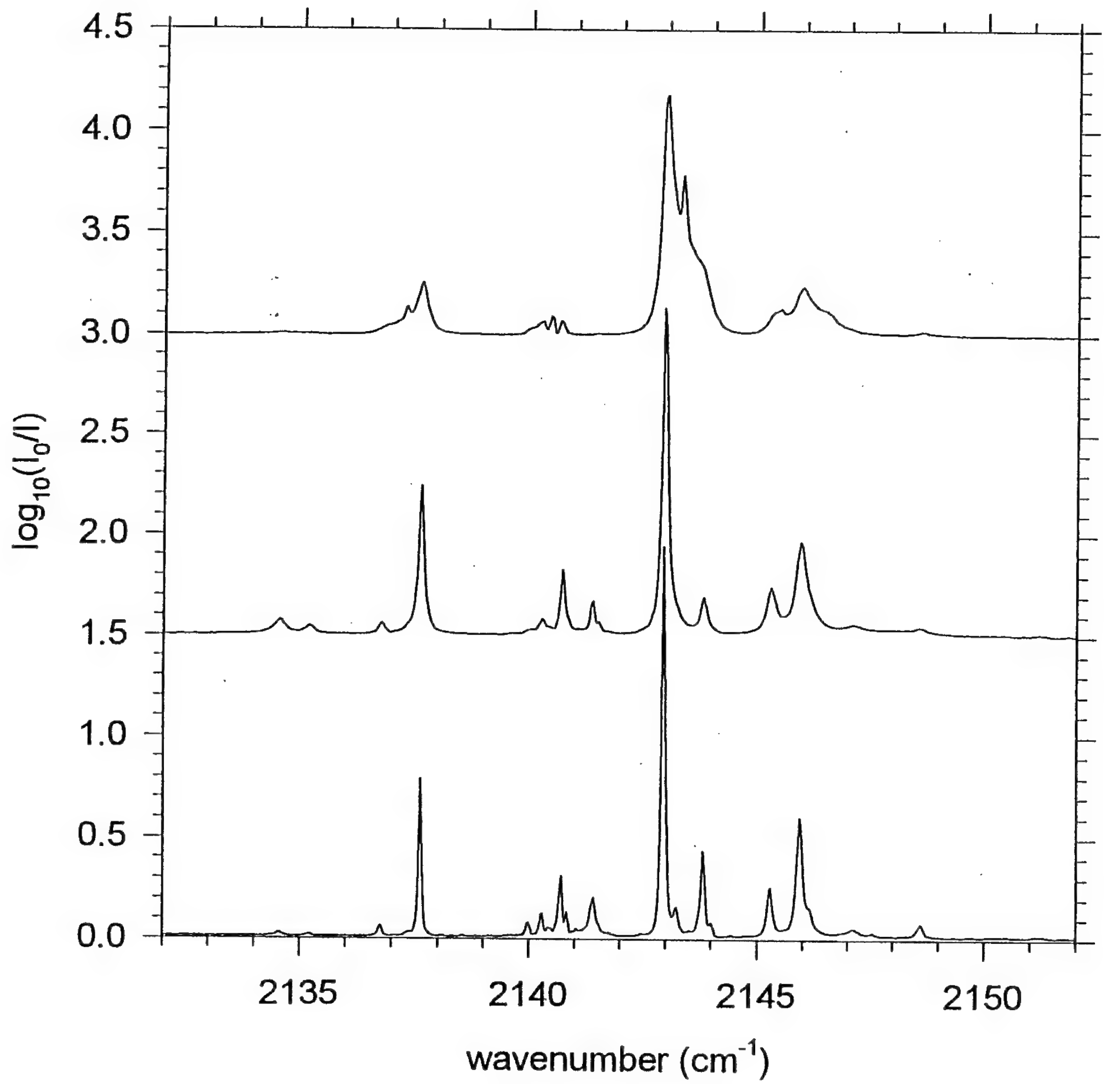
Deposition Cartoon



Experimental Diagram – Sample Deposition



IR Absorptions of CO/pH_2



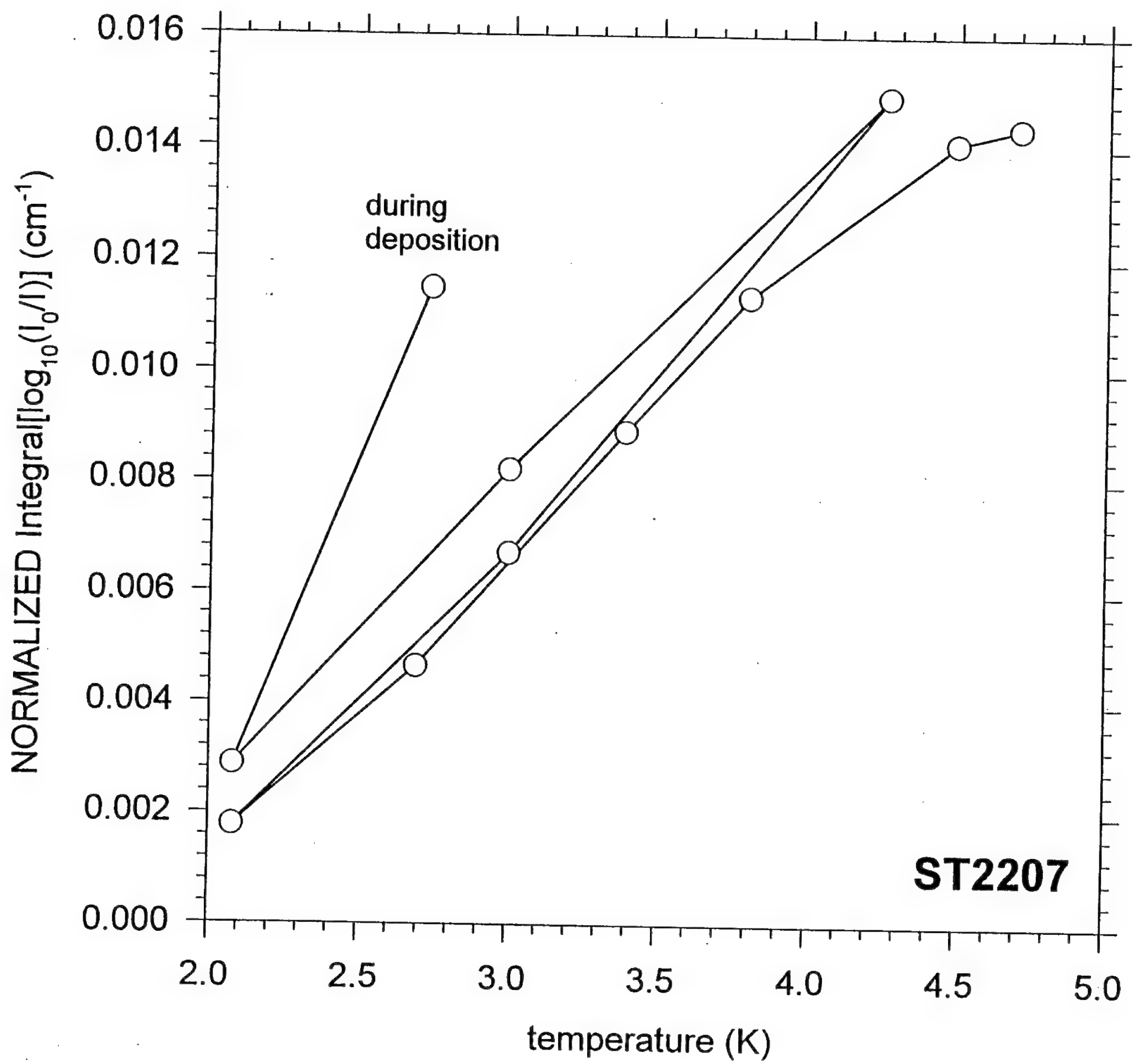
75 PPM CO/pH2
d = 1.7 mm
resolution = 0.1 cm^{-1}

as deposited at 2 K
(probably hcp+fcc)

warmed to 4 K

after anneal, at 2 K
(pure hcp?)

Intensity of 2135 cm^{-1} band vs. Temperature

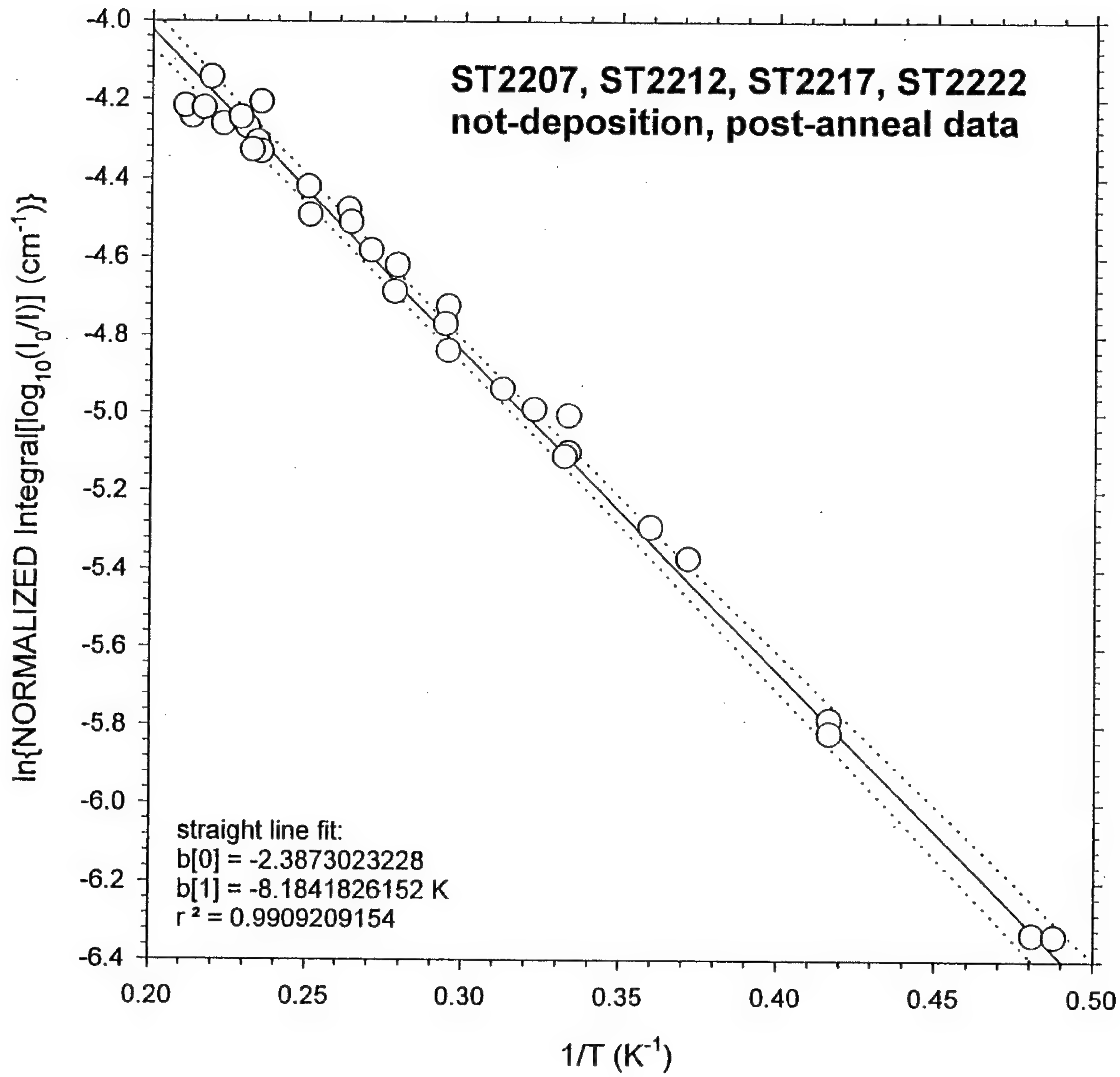


0.9 mm CO/pH_2 layer deposited on top of 1.9 mm pure pH_2 layer.

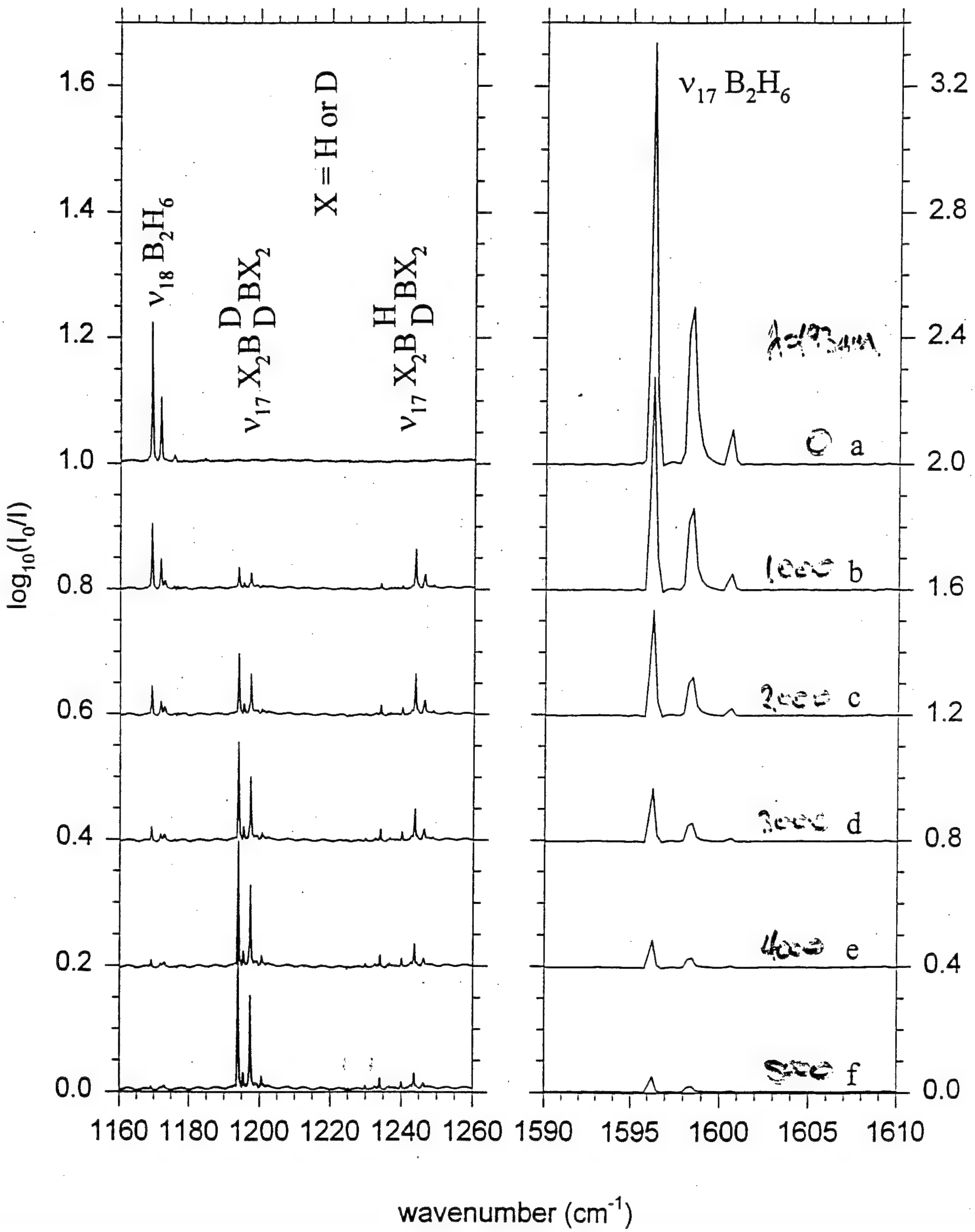
Integrated intensity of 2135 cm^{-1} band normalized to integral over entire CO band for as-deposited sample.

Irreversible shift upon annealing attributed to fcc → hcp conversion (introduces T measurement error ≈ +0.2 K).

"Van't Hoff Plot"

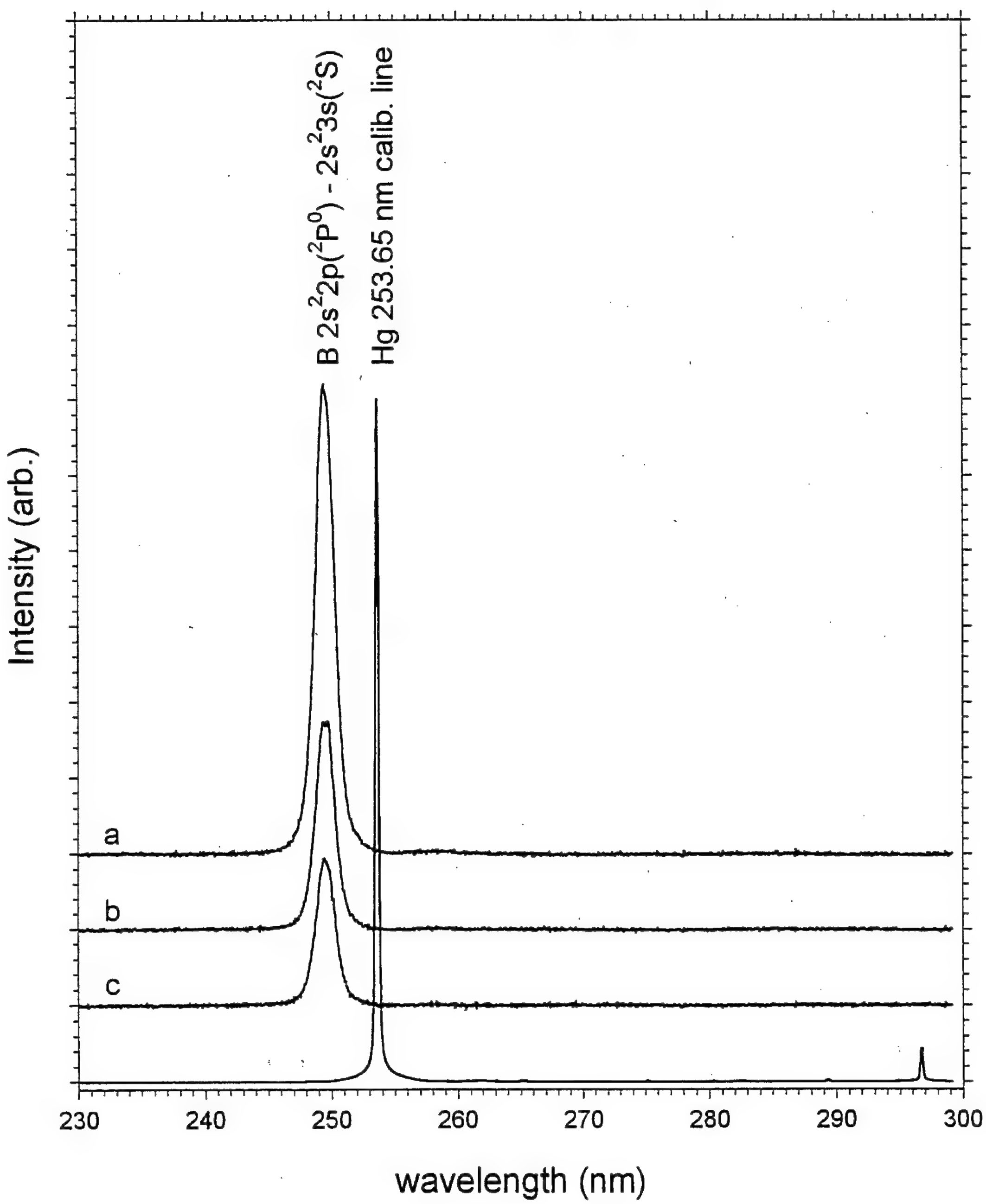


st2345, diborane/oD$_2$ (20 ppm)

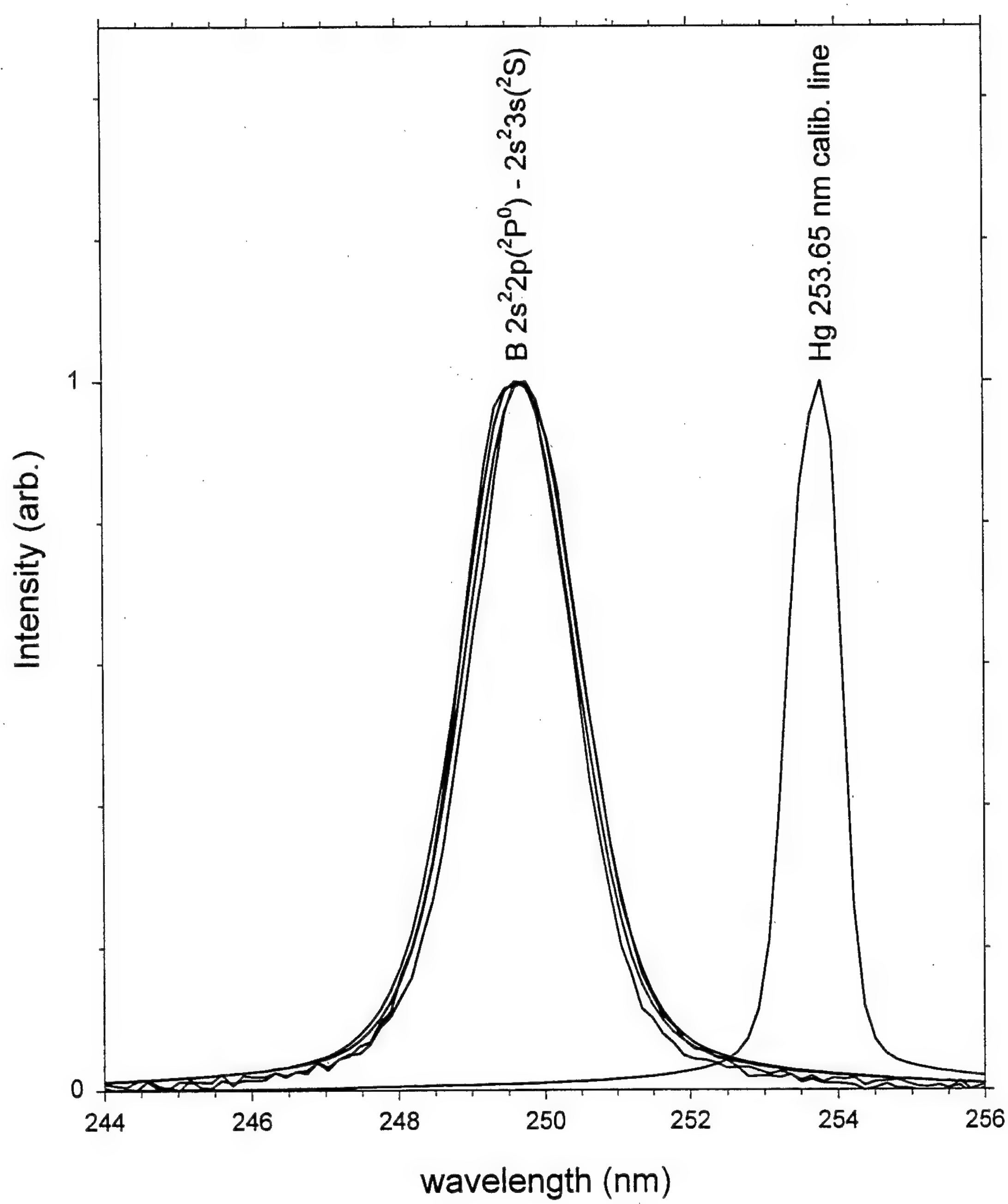


B/pH$_2$ LIF

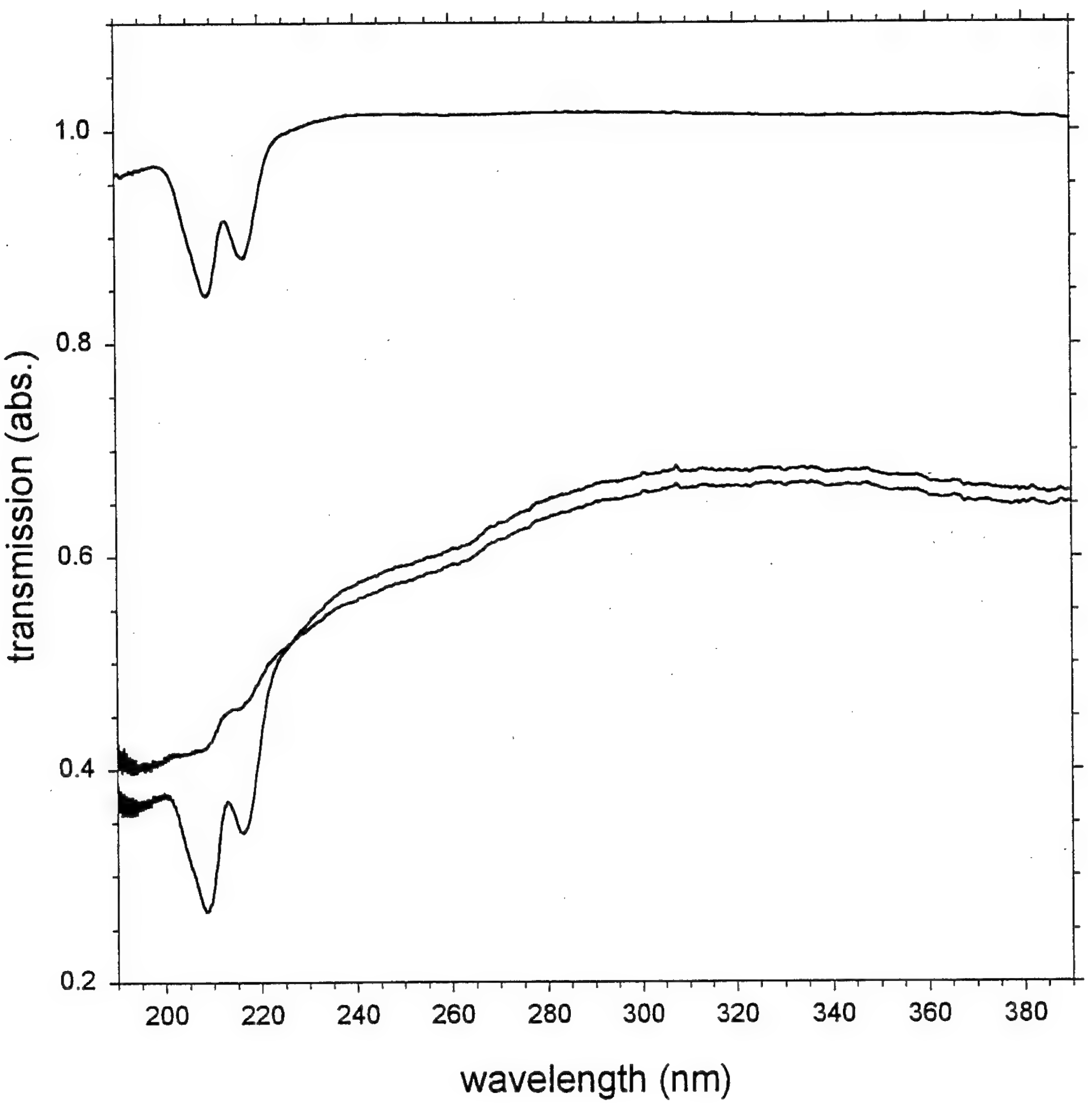
λ_{exc} = 217 nm, 125 μJ/pulse



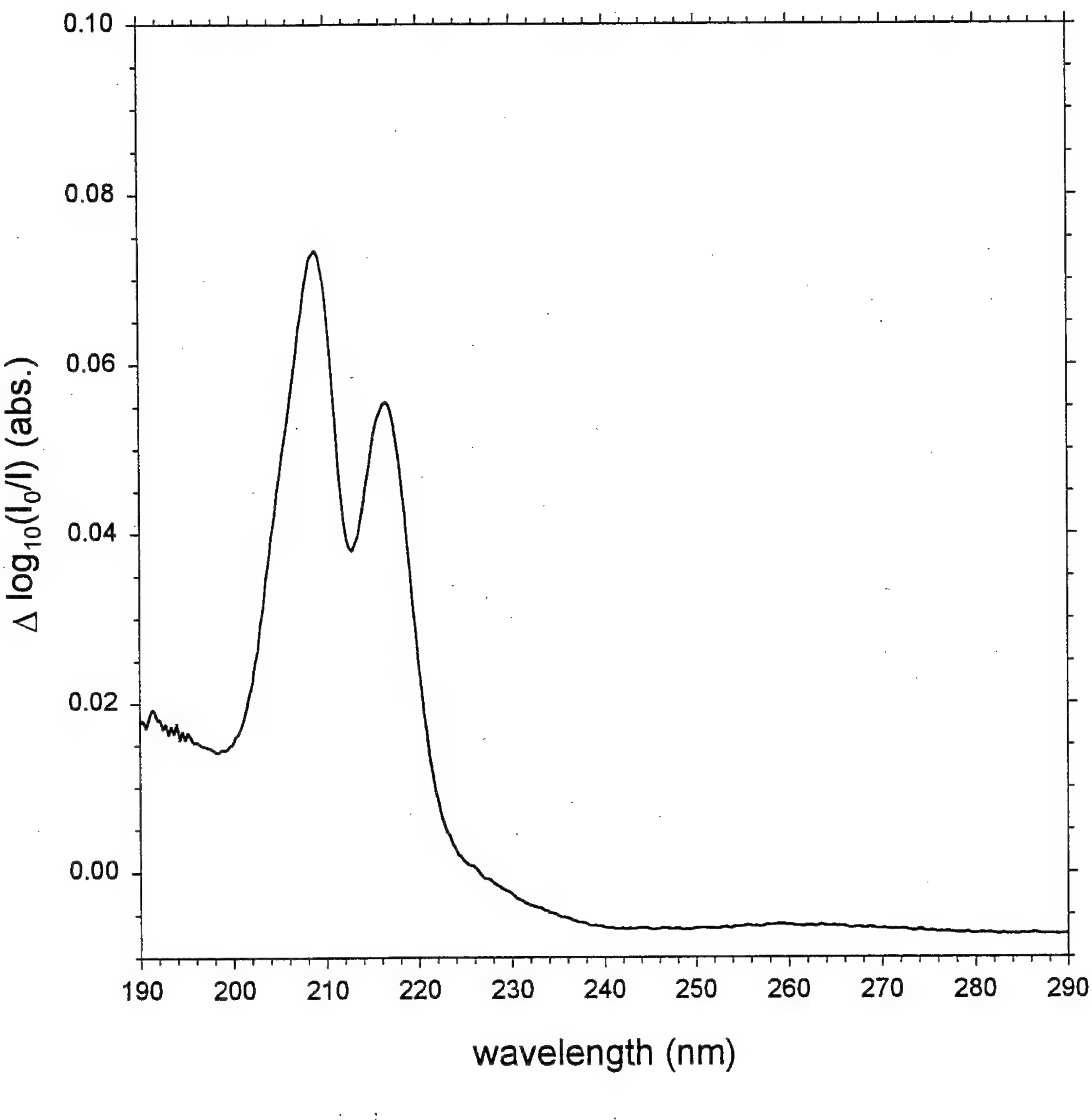
B/pH$_2$ LIF
λ_{exc} = 207, 210, 217, and 220 nm



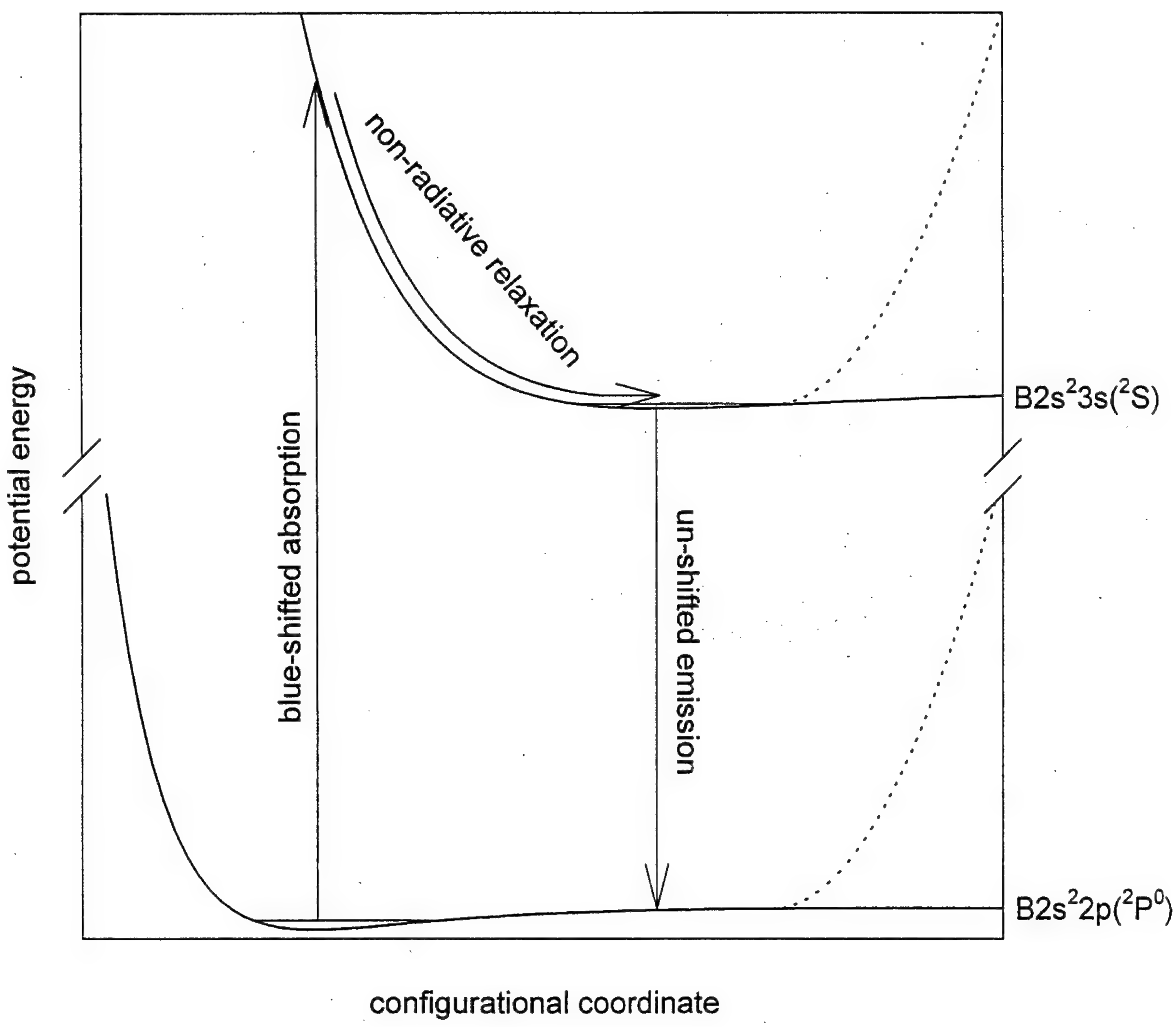
B/pH$_2$ UV absorption and photobleaching



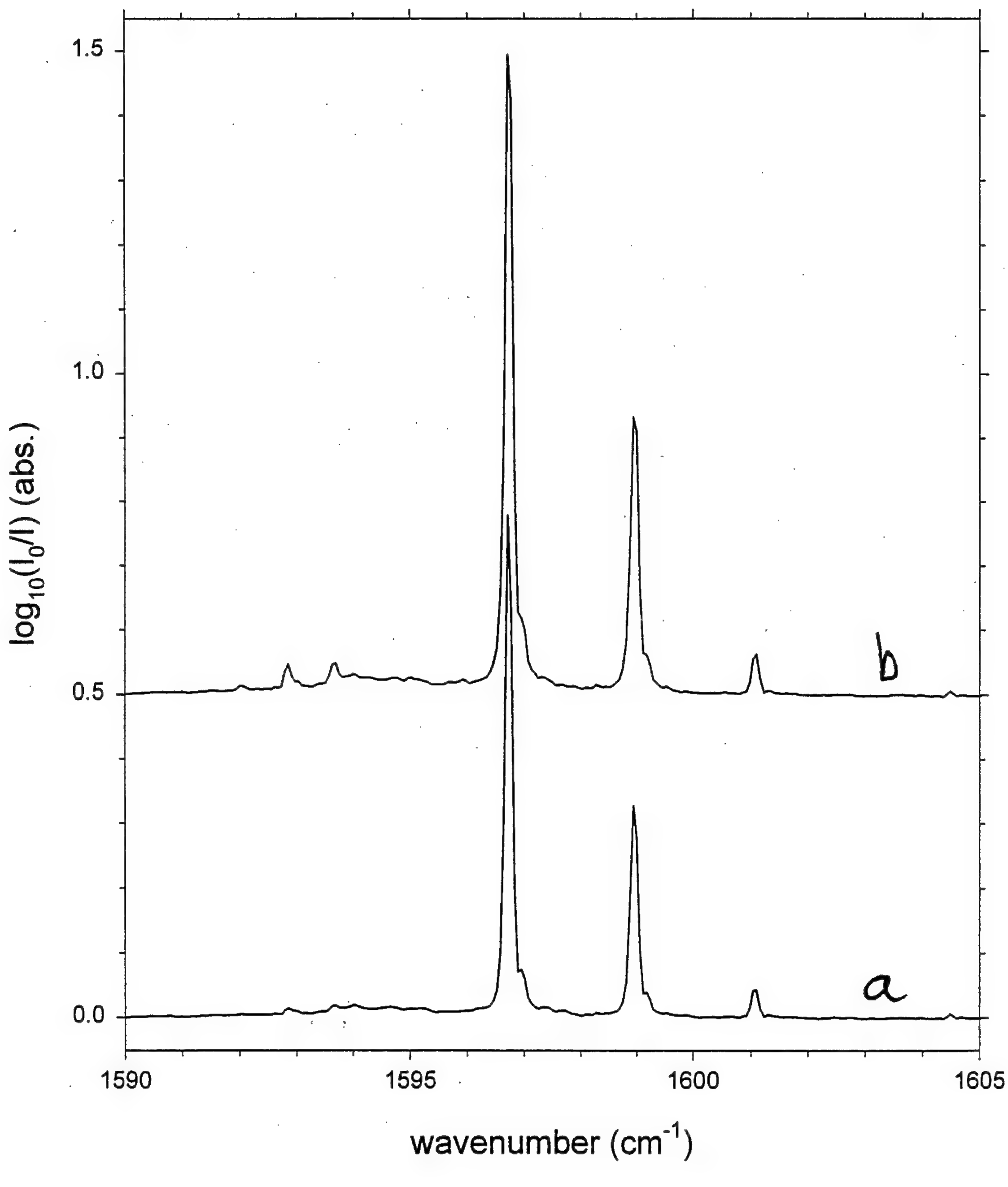
B/pH_2 UV photobleached lineshape



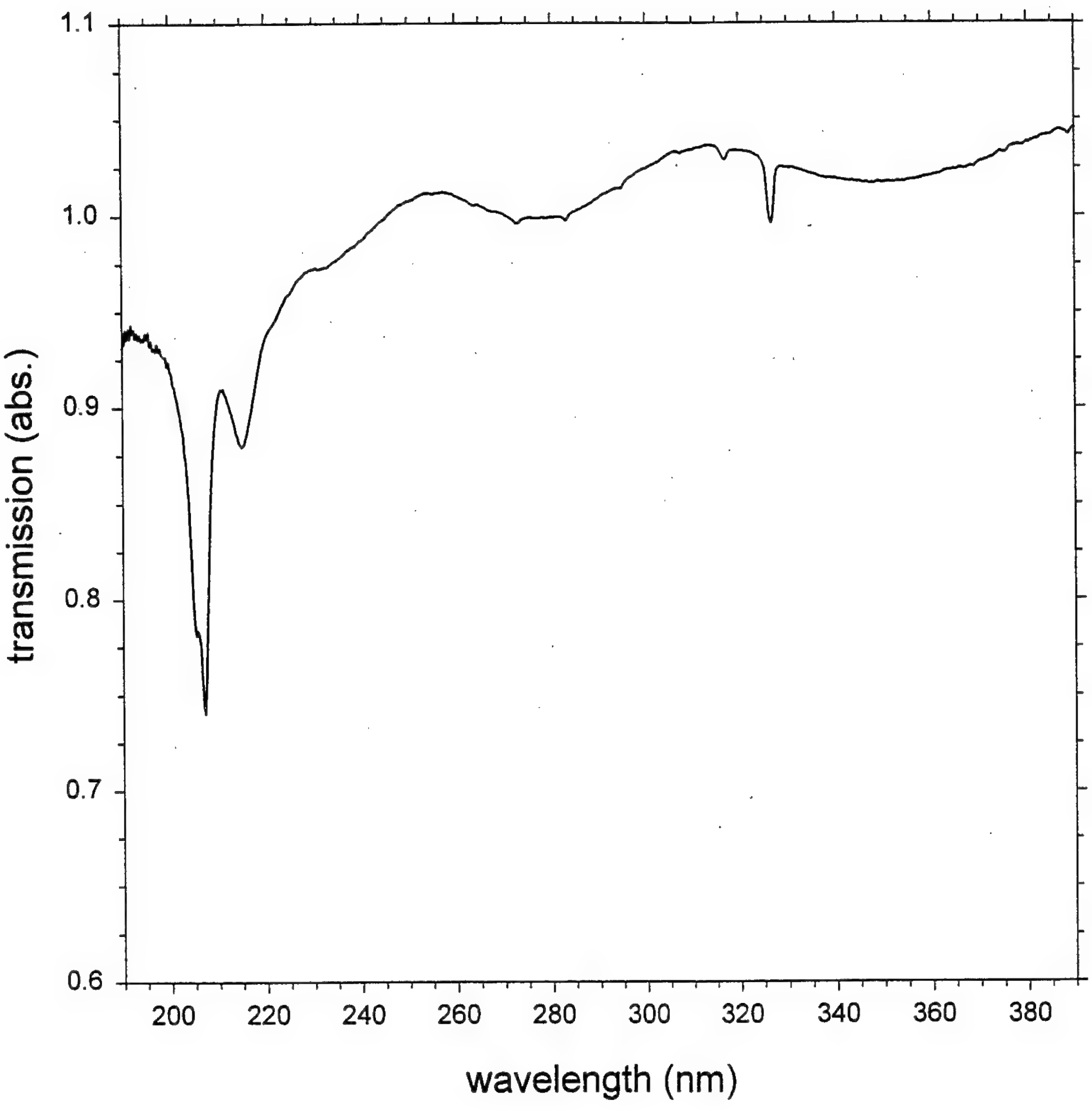
B/pH$_2$ LIF Cartoon



ν_{17} B_2H_6 in B/pH_2 solid
as deposited and photobleached

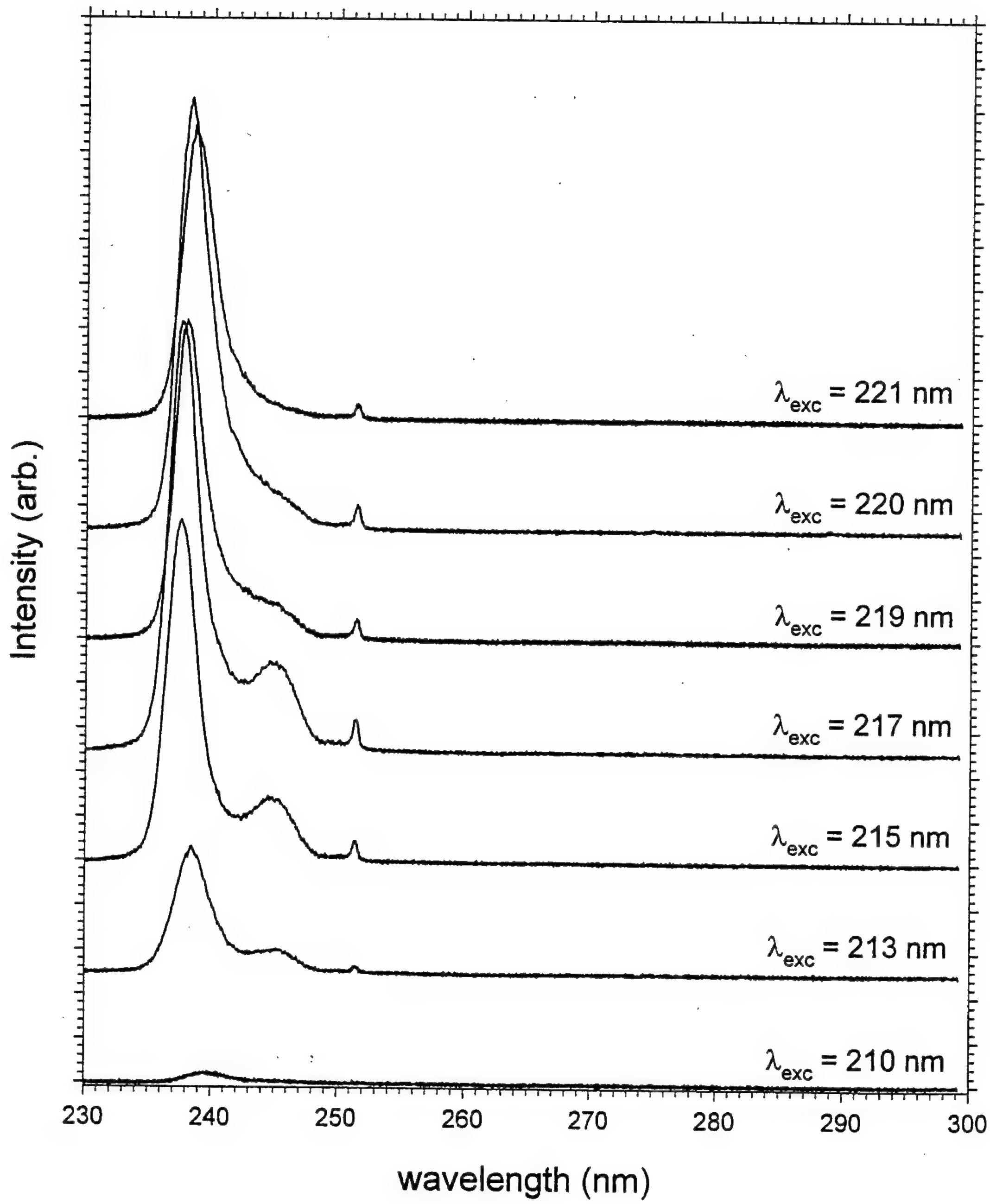


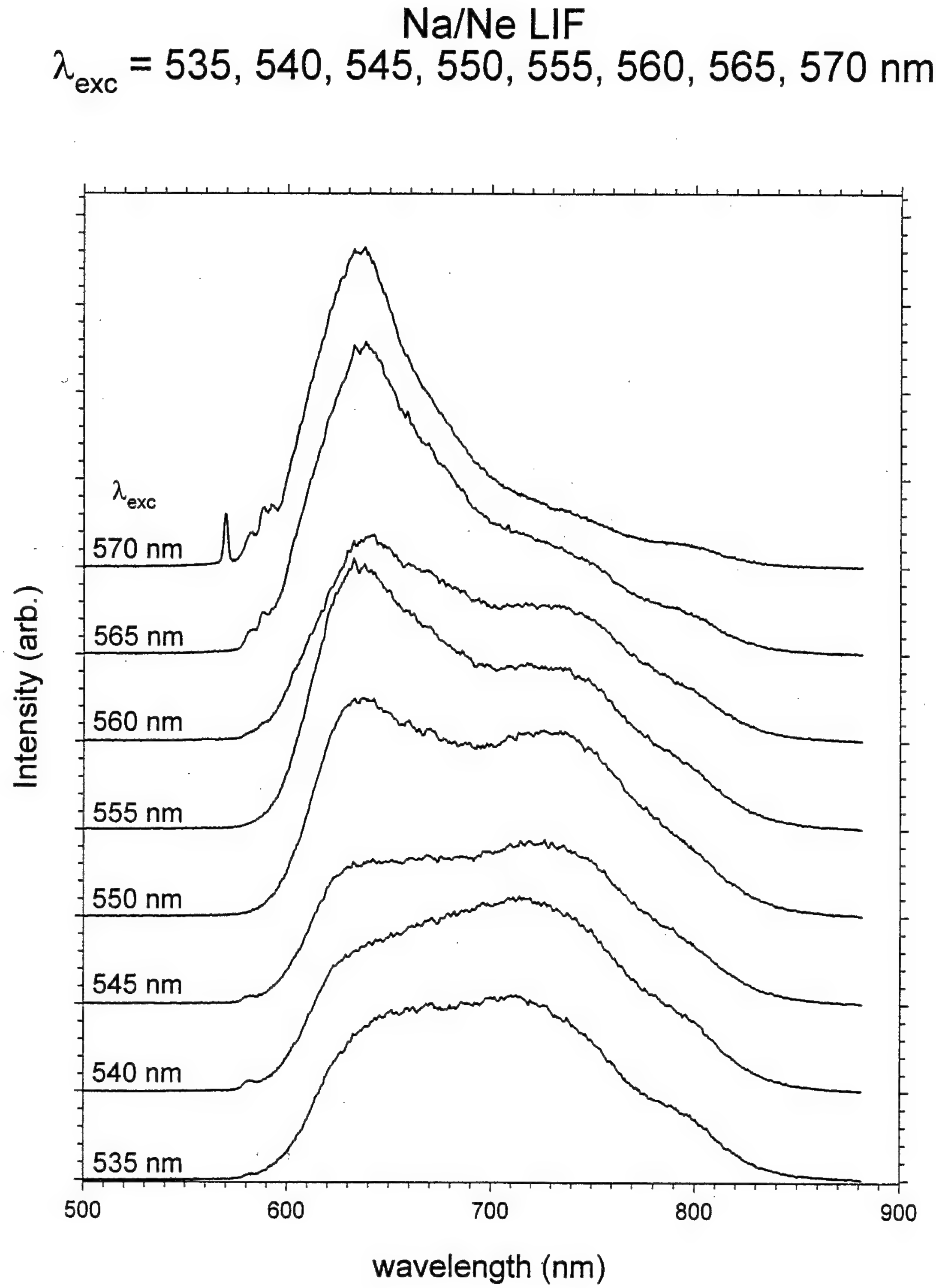
B/Ne UV absorption



B/Ne LIF

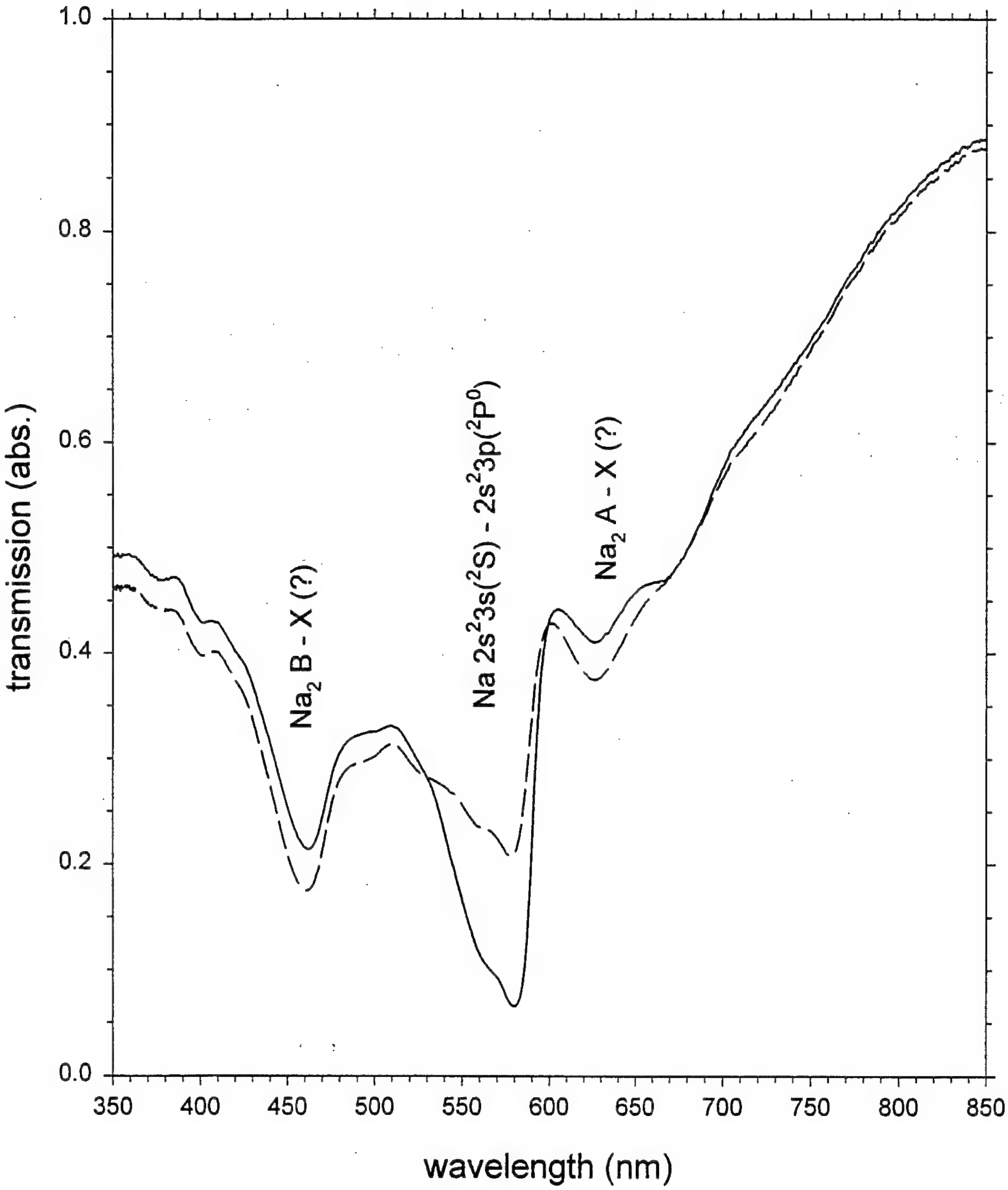
λ_{exc} = 210, 213, 215, 217, 219, 220, 221 nm



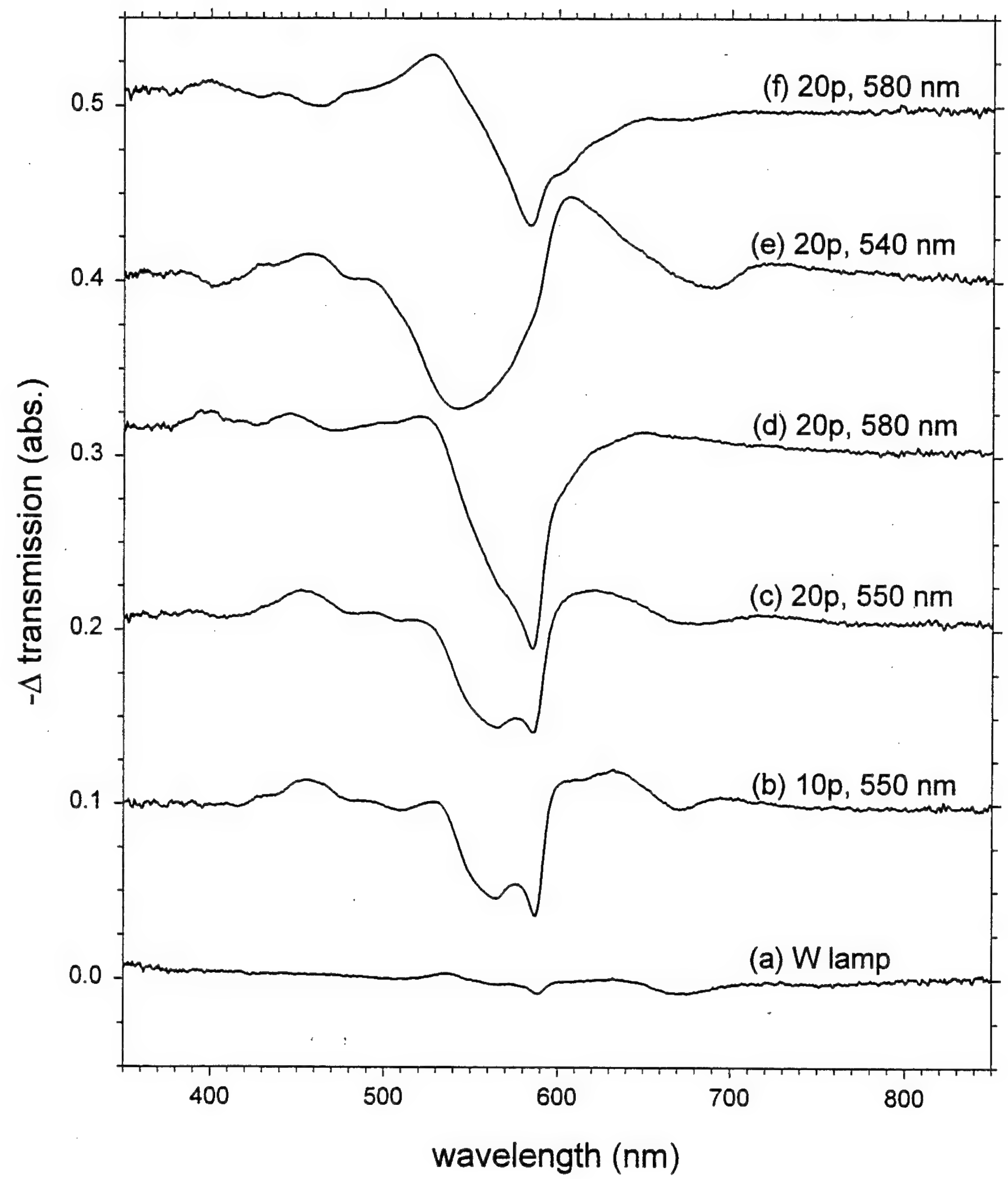


Na/Ne LIF
λ_{exc} = 535, 540, 545, 550, 555, 560, 565, 570 nm
λ_{exc}
570 nm
565 nm
560 nm
555 nm
550 nm
545 nm
540 nm
535 nm
Intensity (arb.)
500
600
700
800
900
wavelength (nm)

Na/pH$_2$ transmission spectrum
as deposited and photobleached



Na/pH_2 photobleaching
60 to 90 μJ/pulse, $d_{spot} \approx 4$ mm



Conclusions

* As-deposited pH_2 samples are mixed hcp/fcc close-packed solids that transform to hcp upon annealing to ≈ 5 K.

* Demonstrated trapping of various dopant atoms, molecules, and ionic species using conventional matrix isolation sources.

* Some dopant IR absorption bands show unresolved structure even at 0.1 cm^{-1} resolution.

* Measured ~ 1 K temperature rises in ~ 0.1 cm thick samples subjected to 10 mW/cm^2 heat loads during deposition; estimated thermal conductivity of rapid vapor deposited pH_2 is ~ 1 mW/cm-K.

* Observed guest-host photochemistry during attempts to produce energetic dopants via 193 nm irradiation.

* Observed LIF of B atoms in solid pH_2. Emission lineshape is independent of excitation wavelength. Photobleaching results in uniform changes to absorption lineshape.

* LIF of Na atoms in solid pH_2 is at least four orders of magnitude weaker than LIF of Na atoms in solid Ne. Photobleaching effect depends on excitation wavelength and produces varying changes to absorption lineshape.

Future Directions

* Bruker IFS120HR on order.

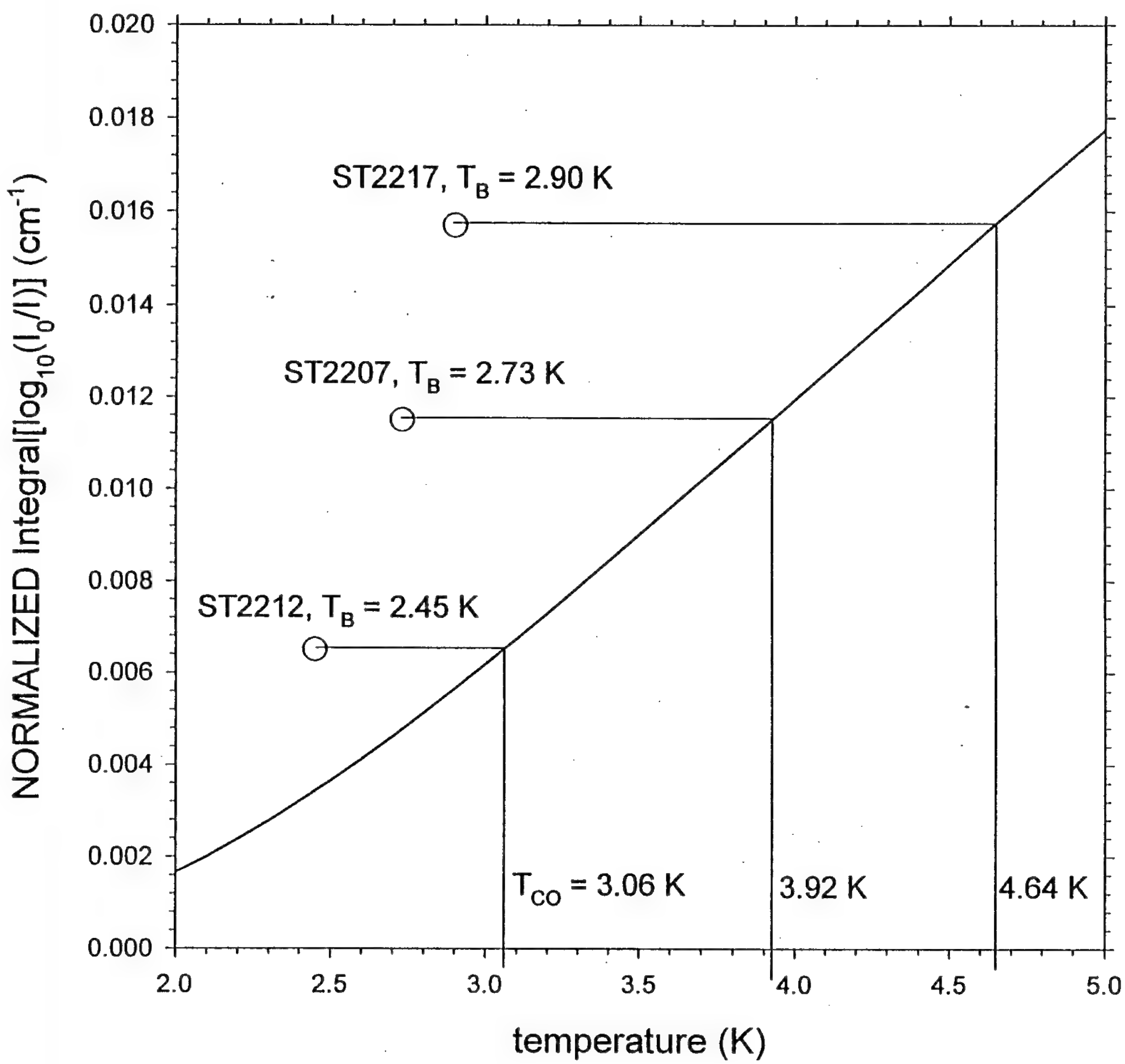
* High resolution IR absorption (0.003 cm^{-1}) and Raman (0.05 cm^{-1}) spectroscopies:
    - unresolved rotational (hindered rotor?) structure in presently available spectra.
    - determine inhomogeneities in dopant environment:
        - hcp/fcc vs. random stacked for as-deposited
        - dopant-dopant interactions (clusters).

* Analysis and simulation of IR spectra:
    - dopant absorptions
        - CO/pH_2 "crystal field" model
            - (collaboration with T. Momose, Kyoto U)
        - direct simulation given dopant-H_2 potentials.
    - induced H_2 absorptions

* Measure fluorescence decay of "B atom" LIF.

* Work to increase dopant concentrations from 0.1 to 1% levels; demonstrate useful energy storage.

Substrate and Bulk Hydrogen Temperatures During Deposition



"thermometer curve:"

$y = A \exp[-E/T]$

$A = 0.08602$

$E = 7.896$ K

Prior to depositions

$T_B = 1.89(\pm 0.02)$ K

After depositions

$T_B = 2.08(\pm 0.05)$ K

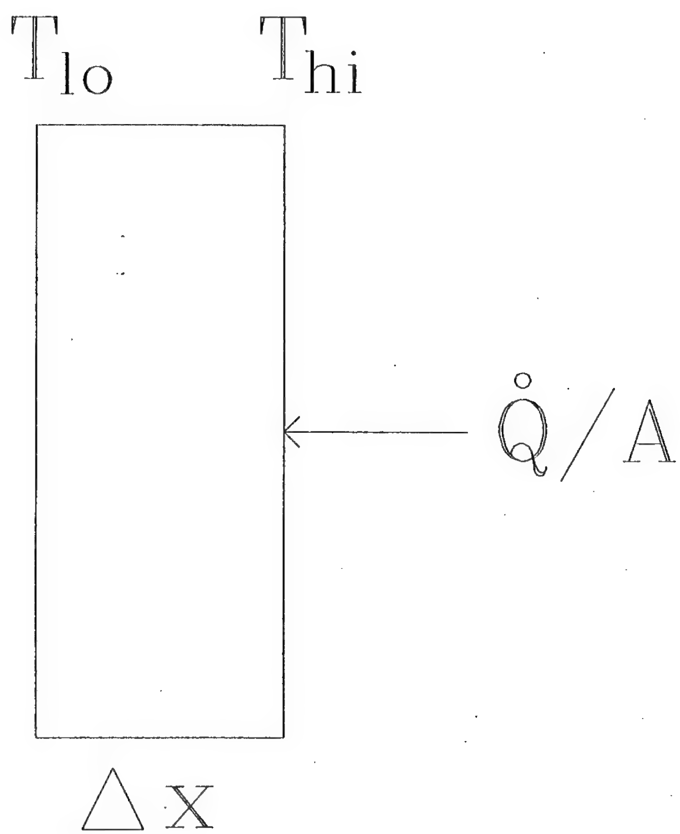
pH_2 inlet & deposition rates:

ST2212: 110 mmol/hr
26 µm/min

ST2207: 200 mmol/hr
48 µm/min

ST2217: 240 mmol/hr
55 µm/min

1-D Heat Transfer



$\dot{Q}/A = -\kappa\, \Delta T/\Delta x$

$\Delta T = T_{hi} - T_{lo}$

κ is the thermal conductivity

units:

$\dot{Q}/A$ (mW/cm^2)

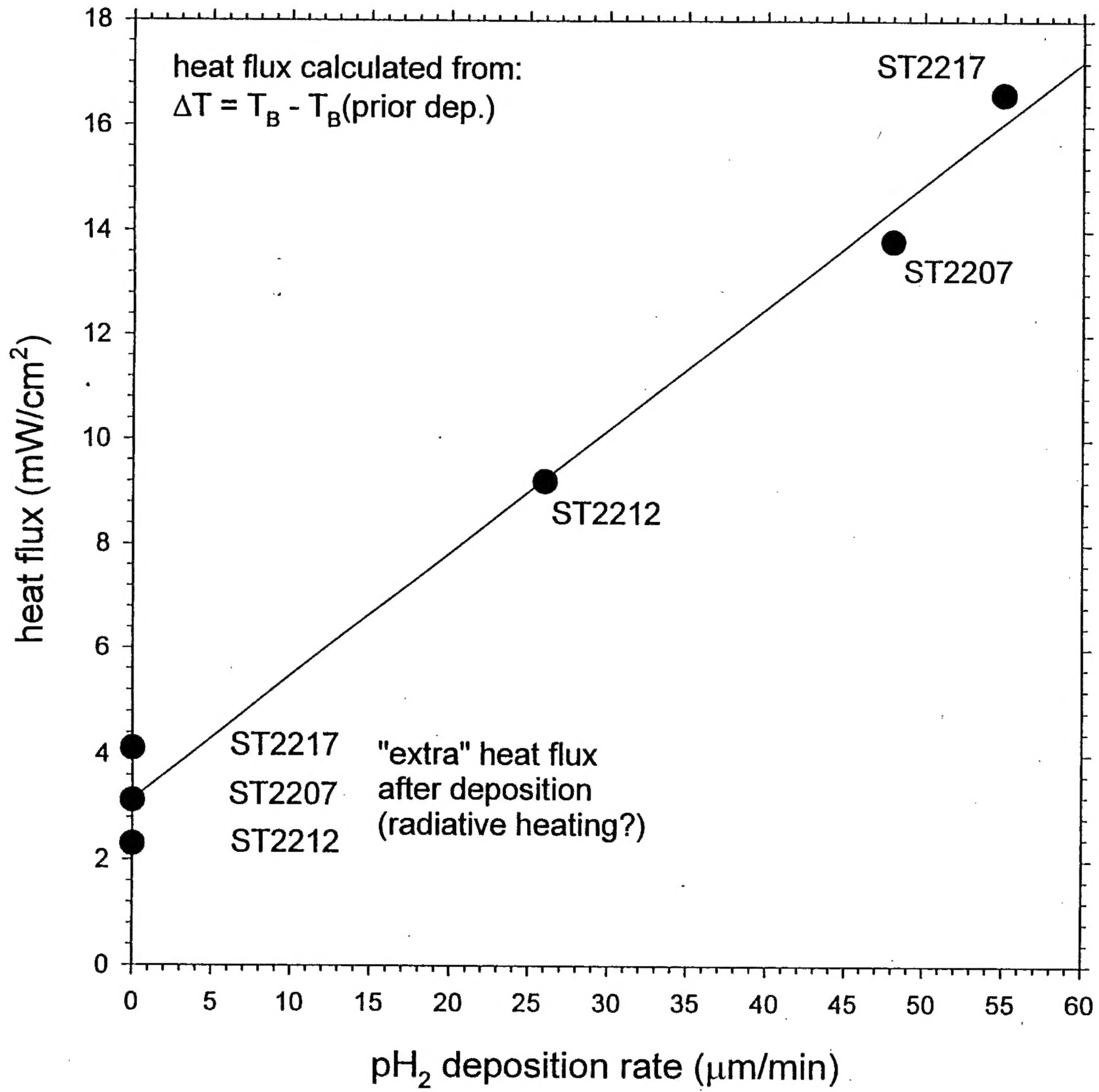
ΔT (K)

Δx (cm)

κ (mW/cm-K)

note: 1 mW/cm-K = 0.1 W/m-K

Calculated Heat Flux vs. pH_2 Deposition Rate



Total deposition heat fluxes:

ST2212 9.2 mW/cm^2

ST2207 13.8 mW/cm^2

ST2217 16.6 mW/cm^2

Total – extra:

ST2212 6.9 mW/cm^2

ST2207 10.7 mW/cm^2

ST2217 12.5 mW/cm^2

Slope of fit line $\Rightarrow$

$E_{dep}(pH_2) = 3.25$ kJ/mol

(390 K)

Compare with:

$E_{sub}(pH_2) = 0.9$ kJ/mol

(110 K)

Thermal Conductivity of Rapid Vapor Deposited pH_2

Expt.	$[T_{CO} - T_B]$ (K)	Δx (cm)	$\dot{Q}/A$ (mW/cm^2)	κ (mW/cm-K)	κ (W/m-K)
ST2212	0.61	0.12	9.2	1.8	0.18
ST2207	1.19	0.22	13.8	2.6	0.26
ST2217	1.74	0.25	16.6	2.4	0.24

Expt.	$[T_{CO} - T_B]$ (K)	Δx (cm)	$\dot{Q}/A$ (mW/cm^2)	κ (mW/cm-K)	κ (W/m-K)
ST2212	0.61	0.12	6.9	1.4	0.14
ST2207	1.19	0.22	10.7	2.0	0.20
ST2217	1.74	0.25	12.5	1.8	0.18

Comparison with Literature TC Values

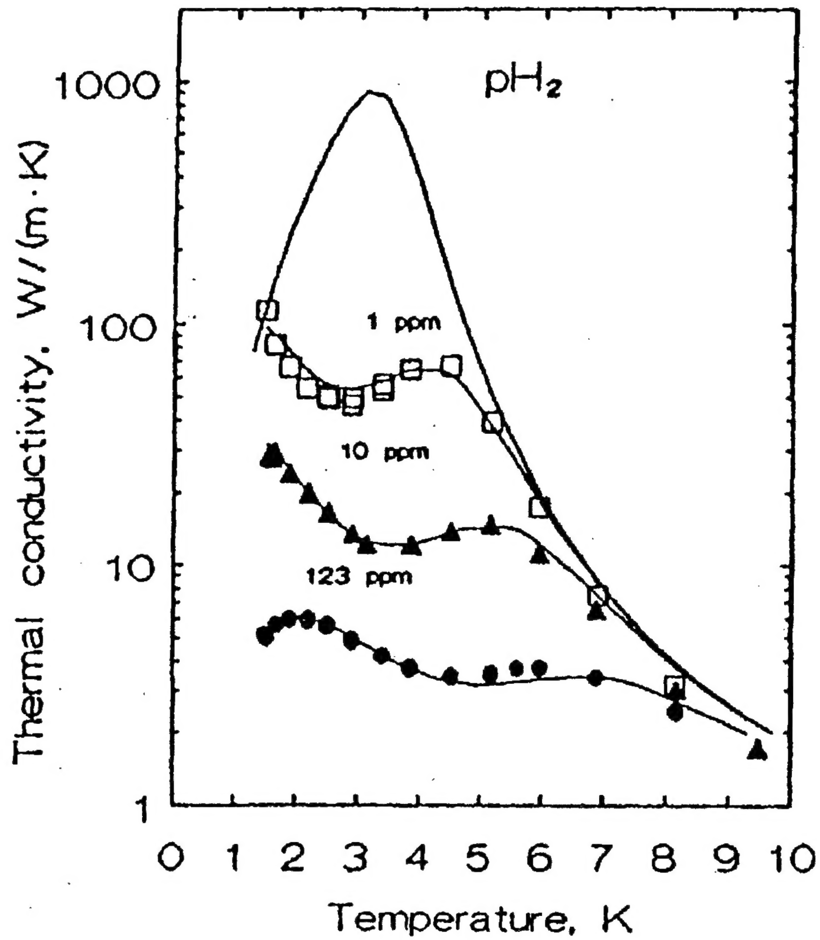


FIG. 1. Thermal conductivity of crystals of pure pH_2 and pH_2 with Ne impurity (the concentration in ppm are indicated); the solid lines are calculated results.

Previous studies on pH_2 single crystals grown from the gas phase in an enclosed cell near 10 K.

V.G. Manzhelii, B.Ya. Gorodilov, and A.I. Krivchikov, "Heat transfer in solid parahydrogen with heavy impurities (neon, argon)," Low Temp. Phys. v22, p131 (1996).

ST2330a&b
1100 PPM O_2/pH_2
photolyzed at 193 nm